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IN ALL ITS APPLICATIONS TO

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EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

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THE CHEMICAL NEWS.

VOLUME CII.

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No. 2640.—JULY 1, 1910.

THE DEVELOPMENT OF THE ATOMIC THEORY.

II.—The Various Accounts of the Origin of Dalton's Theory.

By ANDREW NORMAN MELDRUM, D.Sc.
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The origin of Dalton's theory remains one of the outstanding problems in the history of chemistry. Yet the amount of material at hand for the study of the subject is considerable. Dalton's note-books, discovered within the last twenty years in the rooms of the Manchester Literary and Philosophical Society, contain material of the highest value for the purpose. Also, there are on record important accounts of the genesis of the theory by three different persons. One is given by William Charles Henry, another by Thomas Thomson, and another by Dalton himself. Although there are yet other accounts these three are the only ones that need be considered in detail in this paper.

The main object of the paper is to offer a suggestion, by way of explanation of how these various accounts arose, and to that extent of the discrepancies between them. It will become more and more evident in the course of the paper that Dalton is the person responsible for these discrepancies.

1. *The Influence of J. B. Richter.*

William Charles Henry was the pupil, the friend, and finally the biographer of Dalton. He held a conversation with Dalton on the subject of the origin of the theory, in which special importance was given to the influence of J. B. Richter. "The speculations which gave birth to the atomic theory were first suggested to Mr. Dalton by the experiments of Richter on the neutral salts . . . a table was formed exhibiting the proportions of the acids and the alkaline bases constituting neutral salts. It immediately struck Mr. Dalton that if these saline compounds were constituted of an atom of acid and one of alkali, the tabular numbers would express the relative weights of the ultimate atoms, These views were confirmed and extended by a new discovery of Proust," &c. (W. C. Henry, "Memoirs of Dalton," p. 84).

This narrative received strong support from William Henry (the father of W. C. Henry), who held more than one conversation with Dalton on the subject. The following is part of a minute, dated February 13, 1830, of one of these conversations:—"Confirmed the account he before gave me of the origin of his speculations leading to the doctrine of simple multiples, and of the influence of Richter's table in exciting these views" (*Ibid.*, p. 63).

The Henrys, father and son, are entitled to the fullest credence in this matter. Their acquaintance with Dalton was more intimate than that of any other man of science, Peter Clare excepted. In the preface to his biography of Dalton, W. C. Henry refers with just pride to Dalton's "almost lifelong friendship with my father, never shadowed by even a passing cloud"; and he refers also to "his early favourable notice of and unceasing benevolent regard towards myself, thoughtfully manifested in his last bequest to me of what he had most prized in life." This was the bequest of all his chemical and philosophical instruments and apparatus. Further illustration of this friendship is to be found in the dedication of Dalton's "New System of Chemical Philosophy" (vol. i., Part 2) to William Henry (along with Humphry Davy), and of Henry's "Elements of Experimental Chemistry" (6th Ed., 1810) to Dalton.

There is no room for doubt that the reports of these conversations with Dalton are perfectly authentic. W. C. Henry states that he noted down Dalton's expressions "immediately after each lesson," and the passage which has been quoted, regarding the influence of Richter, is copied, he says, "verbatim from my own journal when his pupil" (*Ibid.*, p. 84). Nevertheless, Henry knew there was something wrong. The date of his conversation with Dalton was February 5, 1824, and he says, "on reviewing in conversation, after the lapse of twenty years, the labours of the past, Dalton himself may have failed in recalling the antecedents of his great discovery in the exact order of sequence" (*Ibid.*, p. 86).

Again, the Richter story is strongly challenged by Thomas Thomson. "When I visited him in 1804 at Manchester both Mr. Dalton and myself were ignorant of what had been done by Richter on the same subject." Again, "Nobody knows better than myself that Dalton was ignorant of what Richter had done about ten years before him" (*Proc. Phil. Soc. Glasgow*, 1845-6, ii., pp. 86, 88). This shows conclusively that Dalton said nothing about Richter to Thomson.

Now that we have access, thanks to Roscoe and Harden's "New View of the Origin of Dalton's Atomic Theory," to the valuable material contained in Dalton's notebooks, we can carry the critical process further than Henry and Thomson did. The notebooks show, as Roscoe and Harden point out, that Dalton had been busily engaged during the year 1803 on the atomic theory, and that he was investigating the non-metallic elements then, and not Richter's acids and bases at all. The date of the earliest reference to Richter is April 19th, 1807 (Roscoe and Harden, "New View of the Origin of Dalton's Atomic Theory," p. 79; see also pp. 7—10, 46, 91—94). There is really no room for doubt that Dalton's declarations in 1824 and 1830 to one and the same effect regarding the influence of Richter must be set aside (Roscoe and Harden, *loc. cit.*).

2. *The Composition of Marsh-gas and Olefiant Gas.*

Thomas Thomson says that the theory first occurred to Dalton during his investigation of marsh-gas and olefiant gas. The discovery of the composition of these gases led to the discovery of the law of multiple proportion, and the theory was then devised in order to explain the law. His exact words are:—

"Mr. Dalton informed me that the atomic theory first occurred to him during his investigations of olefiant gas and carburetted hydrogen gas, at that time imperfectly understood, and the constitution of which was first fully developed by Mr. Dalton himself. It was obvious from the experiments which he made upon them that the constituents of both were carbon and hydrogen, and nothing else. He found, further, that if we reckon the carbon in each the same, then carburetted hydrogen contains exactly twice as much hydrogen as olefiant gas does. This determined him to state the ratios of these constituents in numbers, and to consider the olefiant gas a compound of one atom of carbon and one atom of hydrogen; and carburetted hydrogen of one atom of carbon and two atoms of hydrogen. The idea thus conceived was applied to carbonic oxide, water, ammonia, &c., and numbers were given representing the atomic weights of oxygen, azote, &c., deduced from the best analytical experiments which chemistry then possessed (Thomas Thomson, "History of Chemistry," ii., 291).

This narrative has passed muster for many years. It was accepted with reservations by W. C. Henry ("Memoir of Dalton," p. 80) and Angus Smith ("Memoir of Dalton," p. 231), and by Roscoe and Schorlemmer without objection ("Treatise on Chemistry, Non-metallic Elements," 1877, p. 36). It is of special importance because, more than any other version of the origin, it has influenced the opinion of the generality of chemists.

There is, nevertheless, the best reason for thinking that marsh-gas and olefiant gas did not have the effect which it assigns to them of leading to the theory.

Indeed, in 1811, Dalton connected the theory in its early days with the oxides of nitrogen:—"I remember the strong impression which at a very early period of these inquiries was made by observing the proportion of oxygen to azote, as 1, 2, and 3, in nitrous oxide, nitrous gas, and nitric acid, according to the experiments of Davy" (*Nicholson's Journ.*, 1811, xxix., 143). Thomson must have seen the necessity of abandoning the marsh-gas and olefiant gas story, for he said in 1850:—"Dalton founded his theory on the analysis of two gases, namely, protoxide and deutoxide of azote" (*Proc. Phil. Soc. Glasgow*, 1850, iii., 140).

Roscoe and Harden (*loc. cit.*, p. 28) point out that Dalton had been busily engaged on the theory the year before he investigated these gases. He had even arrived at the fundamental ideas of his system, and had constructed a table of atomic weights by September 6th, 1803.

Obviously, Thomson's account of the origin of the theory is untrustworthy, inasmuch as marsh-gas and olefiant gas had no part in the matter. The question arises, who is responsible for the error, Thomson or Dalton? Before answering this question it is necessary to consider carefully the relations between the two men and the circumstances under which Thomson's narrative arose.

Thomson, unlike the Henrys, was not a personal friend of Dalton. He had made an adverse criticism of a certain theory of which Dalton was the author, and the author had made a stiff rejoinder (see *Nicholson's Journ.*, 1804, viii., 145; and *Annals of Philosophy*, 1814, iv., 65). He thereupon paid a visit to Manchester with the object of arriving at a full understanding of the matter in question. The date of the interview was August 27th, 1804, and it was then, by a fortunate accident, that Thomson learnt of the chemical atomic theory of Dalton.

Again, it is certain that Thomson and Dalton were not subsequently in frequent communication with one another on the subject. The sketch of the theory, which Thomson published in 1807, was accompanied by the note:—"In justice to Mr. Dalton, I must warn the reader not to decide upon the notions of that philosopher from the sketch which I have given, derived from a few minutes conversation, and from a short written memorandum. The mistakes, if any occur, are to be laid to my account, and not to his; as it is extremely probable that I may have misconceived his meaning in some points" (Thomas Thomson, "System of Chemistry," 3rd Ed., 1807, iii., 425).

Nevertheless, this footnote errs on the side of caution. Thomson showed both zeal and care in the matter, for it strongly interested him. His sketch of the theory, giving the first account of it ever published, was based on notes of what Dalton told him, made during the interview, and only one phrase in it is open to objection.

In the "History of Chemistry," published in 1831, Thomson says:—"I wrote down at the time the opinions which he offered, and the following account is taken literarally from my journal of that date" (Thomas Thomson, "History of Chemistry," ii., 287). Then comes an account of the atomic theory, and on that there follows the passage already quoted, connecting marsh-gas and olefiant gas with the genesis of the theory. Here the question arises, is all this taken from the journal, both the sketch of the theory and of how it arose? Only an examination of the journal can settle this point, but I have not succeeded in ascertaining where it is kept, if, indeed, it is still in existence.

It must be admitted also that Thomson seems to become more and more positive regarding the genesis of the theory as time goes on. The account which I have been considering was published in 1831. Six years earlier he had advanced the same account in a more hesitating way:—"Unless my recollection fails me, Mr. Dalton's theory was originally deduced from his experiments on olefiant gas and carburetted hydrogen" (Thomas Thomson, "An Attempt to Establish the First Principles of Chemistry by Experiment," 1825, i., 11). Yet there is no intrinsic improbability that Thomson's recollection is correct. One cannot doubt that during the interview Dalton was much less interested in the question of origin than in the theory itself. If Thomson inquired about the origin Dalton may have made the inquiry an opportunity of expounding the theory in terms of its latest triumph, namely, the composition of marsh-gas and olefiant gas.

3. *The Amended Theory of "Mixed Gases."*

There remains for consideration the account which Dalton gave in a lecture at the Royal Institution of London in 1810. It still exists in his own handwriting, and was found, along with his notebooks, in the rooms of the Manchester Literary and Philosophical Society. He begins by discussing his physical atomic theory, which aimed at explaining the diffusion of gases. He entertained two diffusion hypotheses, the first of which originated in 1801, while an amended hypothesis, he says, was formed in the year 1805. He had not at first "contemplated the effect of *difference of size* in the particles of elastic fluids." On consideration, he "found that the *sizes must* be different," and subsequently arrived at a different explanation of the mechanism of diffusion from the one he at first suggested.

He then introduces the subject of the chemical atomic theory:—"The different *sizes* of the particles of elastic fluids under like circumstances of temperature and pressure being once established, it became an object to determine the relative *sizes* and *weights*, together with the relative *number* of atoms in a given volume. This led the way to the combination of gases . . . other bodies besides elastic fluids, namely, liquids and solids, were subject to investigation, in consequence of their combining with elastic fluids. Thus a train of investigation was laid for determining the *number* and *weight* of all chemical elementary principles which enter into any sort of combination one with another" (Roscoe and Harden, *loc. cit.*, pp. 16—17).

This narrative is certainly right on an essential point. It recognises that Dalton had been using a physical atomic theory, from which he passed to a chemical one. Here

there is a common ground of objection to both the communications made by Dalton, to Thomson and Henry respectively. They both ignore the connection, which certainly existed, between the physical and chemical theories. Thomson did not feel this defect, but Henry did. While not denying the influence of Richter, he sums up the evidence on the subject as "unequivocally demonstrating the genesis of the atomic theory as a general physical conception from the study of matter in the *aëriform* condition, and its first practical application in chemistry to *gaseous* bodies, and emphatically to such as combine *in multiple proportions*" (W. C. Henry, *loc. cit.*, p. 84).

There is no question here of extraordinary insight and discernment on Henry's part. He has simply considered the use Dalton had made of the physical atomic theory previous to forming a chemical one. There is therefore not much justification for Roscoe and Harden's suggestion that they had found in Dalton's narrative a *new* view of the genesis of his atomic theory. The view is to be found in Henry, and would be formed by any person who should read with understanding the "Essay on the Constitution of Mixed Gases," which Dalton wrote in 1801.

There is, however, a fundamental objection to Dalton's narrative. It has a deceptive appearance of being historical. Dalton was a pioneer of science, and a pioneer is a man who must make many mistakes and experience many failures. He has taken a number of different scientific movements and marshalled them, so that they are invested with the appearance of a great, irresistible, strategical advance. On examination his narrative, in spite of its grand air, is found to throw much less light than it promises on the line of thought and train of investigation which he pursued. It is excessively abstract in tone, and avoids going into details and particulars and instances. It does not tell us what we want to know most, how and when Dalton arrived at the law of multiple proportions, and the part played by the law in the construction of the theory. Information on these matters is what is wanted, and anything else is beside the point.

Yet there is one novel element in Dalton's account. This is the suggestion that the formation of the chemical atomic theory took place subsequently to the amendment of the diffusion theory. But, as the notebooks show, the chemical theory was formed in 1803. Hence, Roscoe and Harden conclude that 1805, the date which Dalton assigns to his amended diffusion theory, should be 1803 (*Ibid.*, p. 25). Reasons will be given later in a paper on Dalton's theory of "mixed gases" for thinking that the date 1805 is right after all. Hence, Dalton's narrative is doubtful on the only point in which it presents any novelty.

Conclusion.

There are in existence yet other accounts of this matter. One is given by Dalton's pupil, Joseph A. Ransome (W. C. Henry, *loc. cit.*, pp. 220—222), and another by Dalton himself. This was in the lecture which he delivered in Manchester on October 19th, 1835 (*Manchester Times*, October 25, 1835). The main feature which *all* the accounts have in common is that each originated with Dalton. Thomson's narrative and Henry's and Ransome's were based on conversations with him, and there is no ground for impugning their accuracy any more than his good faith. The natural explanation of the existence of so many and various accounts is that Dalton was simply deficient in historical instinct. He did not perceive the difference between describing the genesis of his theory and expounding the theory itself.

A man who makes history as Dalton did need not be a good historian. The account of the origin of the chemical theory in his own handwriting is no more satisfactory than the others which came from him at second-hand. Apparently, Dalton never had in his mind a precise view of how the theory developed, and when invited to give one he produced, on the spur of the moment, an account to which he did, or did not, adhere on the next occasion.

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ON THE CALCULATION OF OPTICO-CHEMICAL CONSTANTS.

Part I.—Aliphatic Hydrocarbons.

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

§ 1. *Introductory.*

It has been pointed out by the author (see "On the Calculation of Thermo-chemical Constants," Arnold, 1909, pp. 1—7) that the usually-adopted method of calculating the specific influences of atoms and unsaturated links on additive physico-chemical properties is fundamentally incorrect, inasmuch as the influences of the ethane and certain other links are ignored. If the influences of these links are not assumed to be zero, the data relative to the subject obtainable in the present state of knowledge reduce to a set of indeterminate equations. The difficulty is overcome and an unjustifiable assumption avoided by the author's general method of calculating physico-chemical constants, which depends upon the use of certain derived constants chosen so as to be obtainable from the indeterminate equations referred to above.

This method has been used successfully for the calculation of thermo-chemical constants. It is now proposed to adopt a somewhat similar procedure in the case of optico-chemical constants. The fundamental constants employed will have, in general, the same general significations as before; but since their specific significations will be entirely different, capital Greek letters will be employed to designate them (instead of small Greek letters as in the case of thermo-chemical constants) in order to avoid any possible confusion.

It has been shown by the author in the monograph referred to above, that, in general, if C represents the influence of a carbon atom irrespective of its valences, H the influence of a hydrogen atom together with the link binding it to carbon, and L_1, L_2, L_3 the influences of the ethane, ethene, ethine links respectively, then the values of C, H, L_1, L_2, and L_3 are not obtainable in the present state of knowledge; but the values of the following derived constants—the so-called "*fundamental constants*"—can readily be calculated:—$A = C + 4H$, $B = 2H - L_1$, $\Gamma = 4H - L_2$, $\Delta = 6H - L_3$. From these constants the theoretical value for any aliphatic hydrocarbon can at once be obtained.

§ 2. *The Data Employed.*

We shall avail ourselves of the experimental work of various chemists. In cases where more than one determination has been carried out on the same substance we shall, as a general rule, choose those results which by their consistency with the main body of data show themselves to be the more accurate. The actual experimental data used in the present paper are exhibited in Table I. In this table, Column 1 gives the number of each substance, by which reference to it can be made; Column 2 gives the name and Column 3 the formula of each substance; Column 4 gives t, the temperature at which each determination was carried out; Column 5 gives d_4^t, the density of each substance at temperature t compared with water at 4° C.; Column 6 gives μ^α, the refractive index of each substance for the α line of the hydrogen spectrum; (= Fraunhofer's C line); Column 7 gives M^α, the *molecular refractivity* for the Hα line calculated according to the formula of Lorentz-Lorenz, according to which $M = \frac{(\mu^2 - 1)m}{(\mu^2 + 2)d}$, where m is the molecular weight of the substance in question; Column 8 gives μ^γ, the refractive index for the Hγ line; Column 9 gives M^γ, the *molecular refractivity* for the Hγ line calculated in a similar manner from μ^γ; Column 10 gives $M^\gamma - M^\alpha$, the *molecular dispersion*; the footnotes give the name of the experimenter to which each result is due, and the references to the original memoirs from which the data have been taken.

TABLE I.

1. No.	2. Substance.	3. Formula.	4. t	5. d_4^t	6. μ^α	7. M^α	8. μ^γ	9. M^γ	10. $M^\gamma - M^\alpha$
1.	Pentane	C_5H_{12}	15·7	0·6251	1·3581	25·30	1·3645	25·71	0·41 (*a*)
2.	Hexane	C_6H_{14}	14·8	0·6645	1·3761	29·70	1·3862	30·41	0·71 (*a*)
3.	Heptane	C_7H_{16}	12·2	0·6903	1·3897	34·32	—	—	— (*b*)
4.	Octane	C_8H_{18}	15·1	0·7074	1·3987	38·95	1·4097	39·90	0·95 (*a*)
5.	Decane	$C_{10}H_{22}$	14·9	0·7278	1·4088	48·21	1·4200	49·37	1·16 (*a*)
6.	Amylene	C_5H_{10}	16·4	0·6664	1·3857	24·65	1·3997	25·45	0·80 (*a*)
7.	Hexylene	C_6H_{12}	15·2	0·6886	1·3965	29·34	1·4093	30·18	0·84 (*a*)
8.	Octylene	C_8H_{16}	16·0	0·7256	1·4137	38·55	1·4274	39·66	1·11 (*a*)
9.	Decylene	$C_{10}H_{20}$	17·0	0·7721	1·4357	47·38	1·4500	48·73	1·35 (*a*)
10.	Valerylene	C_5H_8	20·0	0·6786	1·3976	24·16	1·4130	24·99	0·83 (*c*)
11.	Diallyl	C_6H_{10}	20·0	0·6880	2·3981	28·77	1·4139	29·78	1·01 (*c*)
12.	Heptidine	C_7H_{12}	20·0	0·7458	1·4182	32·46	1·4321	33·39	0·93 (*d*)

(*a*) Landolt and Jahn, *Zeit. Phys. Chem.*, 1892, x., 289.
(*b*) Perkin, *Journ. Chem. Soc.*, 1892, lxi., 287.
(*c*) Brühl, *Liebig's Annalen*, 1880, cc., 139.
(*d*) Brühl, *Liebig's Annalen*, 1886, ccxxxv., 1.

TABLE II.

No.	Substance.	Formula.	M^α.	Increment.	M^γ.	Increment.
1.	Pentane	C_5H_{12}	25·30		25·71	
				4·40		4·70
2.	Hexane	C_6H_{14}	29·70		30·41	
				4·62		
3.	Heptane	C_7H_{16}	34·32		—	4·745 × 2
				4·63		
4.	Octane	C_8H_{18}	38·95		39·90	
				4·63 × 2		4·735 × 2
5.	Decane	$C_{10}H_{22}$	48·21		49·37	
6.	Amylene..	C_5H_{10}	24·65		25·45	
				4·69		4·73
7.	Hexylene	C_6H_{12}	29·34		30·18	
				4·605 × 2		4·74 × 2
8.	Octylene..	C_8H_{16}	38·55		39·66	
				4·415 × 2		4·535 × 2
9.	Decylene	$C_{10}H_{20}$	47·38		48·73	
10.	Valerylene	C_5H_8	24·16		24·99	
				4·61		4·79
11.	Diallyl	C_6H_{10}	28·77		29·78	

TABLE III.

1. No.	2. Substance.	3. Formula.	4. Formula.	5. M^α found.	6. A^α calculated.	7. M^α calculated.	8. Difference between cols. 5 and 7.	9. Error. Per cent.	10. M^γ found.	11. A^γ calculated.	12. M^γ calculated.	13. Difference between cols. 10 and 12.	14. Error. Per cent.
1.	Pentane	C_5H_{12}	5A − 4B	25·30	7·02	25·25	−0·05	−0·20	25·71	6·91	25·77	+0·06	+0·23
2.	Hexane	C_6H_{14}	6A − 5B	29·70	6·85	29·82	+0·12	+0·40	30·41	6·91	30·47	+0·06	+0·20
3.	Heptane	C_7H_{16}	7A − 6B	34·32	[6·90]	34·39	+0·07	+0·20	—	—	—	—	—
4.	Octane	C_8H_{18}	8A − 7B	38·95	6·96	38·96	+0·01	+0·03	39·90	7·00	39·87	−0·03	−0·08
5.	Decane	$C_{10}H_{22}$	10A − 9B	48·21	7·08	48·10	−0·11	−0·23	49·37	7·07	49·27	−0·10	−0·20

Mean A^α = 6·97 Mean A^γ = 6·97
Whence B^α = 2·40 Whence B^γ = 2·27

TABLE IV.

1. No.	2. Substance.	3. Formulæ.	4. Formulæ.	5. Formulæ.	6. $M^\gamma - M^\alpha$ found.	7. $M^\gamma - M^\alpha$ calculated.	8. Difference between cols. 6 and 7.
1.	Pentane	C_5H_{12}	5A′ − 4B′	$4L_1'$	0·41	0·52	+0·11
2.	Hexane	C_6H_{14}	6A′ − 5B′	$5L_1'$	0·71	0·65	−0·06
4.	Octane	C_8H_{18}	8A′ − 7B′	$7L_1'$	0·95	0·91	−0·04
5.	Decane	$C_{10}H_{22}$	10A′ − 9B′	$9L_1'$	1·16	1·17	+0·01

§ 3. *Molecular Refractivities of Saturated Hydrocarbons.*

It is evident from the data tabulated in Table II. that the replacement of hydrogen linked to carbon by a methyl group linked to carbon produces a constant increment in the molecular refractivity, greater in the case of γ-refractivities than in the case of α-refractivities.

From the values of the molecular refractivities given, we can calculate* the mean value of this increment by means of the formula—

$$d = \{5(M_{C_{10}H_{22}} - M_{C_5H_{12}}) + 2(M_{C_8H_{18}} - M_{C_6H_{14}}) + 5(M_{C_{10}H_{20}} - M_{C_5H_{10}}) + 2(M_{C_8H_{16}} - M_{C_6H_{12}}) + (M_{C_6H_{10}} \quad M_{C_5H_8})\} \div 59,$$

where d is the value of this increment—which is an adaptation to the present data of the general formula—

$$d = 6\{(n-1)(x_n - x_1) + (x-3)(x_{n-1} \quad x_2) + \ldots\} \div n(n^2-1),$$

here x_p is the value of the p^{th} term of the series, and n the number of terms—for the determination of the mean value of a constant interval.

This formula gives—

$$d\alpha = (5 \times 22{\cdot}91 + 2 \times 9{\cdot}25 + 5 \times 22{\cdot}73 + 2 \times 9{\cdot}21 + 4{\cdot}61) \div 59 = 269{\cdot}73 \div 59 = 4{\cdot}57,$$

and—

$$d\gamma = (5 \times 23{\cdot}66 + 2 \times 9{\cdot}49 + 5 \times 23{\cdot}28 + 2 \times 9{\cdot}48 + 4{\cdot}79) \div 59 = 277{\cdot}43 \div 59 = 4{\cdot}70.$$

From a large number of experimental data, Brühl (*Zeit. Phys. Chem.*, 1891, vii., 140) calculated the value of this increment for α-refractivities, and obtained the value 4·57 exactly identical with the above. This agreement shows the reliability of the data chosen, and demonstrates clearly the constant value of this increment. In the memoir referred to above, Brühl did not determine the corresponding increment for γ-refractivities, but he came to the conclusion that the corresponding increment in the case of molecular dispersions is constant, and calculated its mean value to be 0·11.

Now, let x be the molecular refractivity of any compound R.H, and y the molecular refractivity of the next higher homologue R.CH_3; then $x\gamma \quad x\alpha$ and $y\gamma - y\alpha$ will be the corresponding molecular dispersions. So that, according to Brühl, $y\gamma - y\alpha - (x\gamma - x\alpha) = 0{\cdot}11$; *i.e.*, $y\gamma - x\gamma = 0{\cdot}11 + y\alpha - x\alpha$; but $y\alpha - x\alpha = 4{\cdot}57$, so that $y\gamma - x\gamma = 0{\cdot}11 + 4{\cdot}57 = 4{\cdot}68$. This value agrees very well with that obtained above, namely, 4·70, which value we shall employ in the present paper.

From Brühl's link-ignoring standpoint, the difference between two adjacent homologues gives the molecular refractivity of a carbon atom plus that of two hydrogen atoms; if, however, we do not assume the influences of the C . H and C . C links to be zero, we must represent this refractivity by the expression $C + 2H - L_1$, *i.e.*, A B. Hence, $A\alpha - B\alpha = 4{\cdot}57$, $A\gamma - B\gamma = 4{\cdot}70$.

Now, the general formula for all saturated chain hydrocarbons is—

$$nC + (2n+2)H + (n-1)L_1 = nA + (1 \quad n)B = (n-1)(A - B) + A.$$

Hence, knowing the values of these hydrocarbons, and of A − B, the values of A can at once be obtained. Thus, pentane is C_5H_{12}; *i.e.*, 5A − 4B. $M\alpha$ for this substance is 25·30, and $M\gamma$ is 25·71. Therefore—

$$A\alpha = 25{\cdot}30 - 4(A\alpha - B\alpha) = 25{\cdot}30 - 4 \times 4{\cdot}57 = 7{\cdot}02;$$
$$A\gamma = 25{\cdot}71 - 4(A\gamma - B\gamma) = 25{\cdot}71 \times 4 \times 4{\cdot}70 = 6{\cdot}91.$$

The values of A calculated thus from each hydrocarbon are shown in Table III. By comparing the four values found for $A\gamma$ with the four corresponding values of $A\alpha$ it appears that $A\alpha = A\gamma$, for, as is evident from Table III., $\Sigma_4 A\alpha = 27{\cdot}91$, $\Sigma_4 A\gamma = 27{\cdot}89$,—such a close agreement is very remarkable. For the mean values we get $A\alpha = 6{\cdot}96$ if the value for heptane is included, or $A\alpha = 6{\cdot}98$ if this value is not taken into account, and $A\gamma = 6{\cdot}97$. We conclude therefore that $A\alpha = A\gamma = 6{\cdot}97$. The values of B can now be calculated, for—

$$B\alpha = A\alpha - (A\alpha \quad B\alpha) = 6{\cdot}97 - 4{\cdot}57 = 2{\cdot}40,$$
$$B\gamma \quad A\gamma - (A\gamma \quad B\gamma) = 6{\cdot}97 - 4{\cdot}70 = 2{\cdot}27.$$

Using these values, namely,—

$$A\alpha = A\gamma = 6{\cdot}97,\ B\alpha = 2{\cdot}40,\ B\gamma = 2{\cdot}27,$$

the molecular refractivities (for both Hα and Hγ lines) of all the saturated hydrocarbons considered have been calculated, and are exhibited together with the differences between them and the experimental, and the percentage errors in Table III. The agreement is very satisfactory.

§ 4. *Molecular Dispersions of Saturated Hydrocarbons.*

An examination of the molecular dispersions of the hydrocarbons might well raise the question whether molecular dispersion calculated according to the formula employed herein is, indeed, an additive property. But if molecular refractivity is additive, then in the nature of things molecular dispersion must also be additive, for it is most improbable that the molecular refractivity found for one particular line of the spectrum should be additive and that for another line not additive; and if both $M\alpha$ and $M\gamma$ exhibit this property, then the difference between them, $M\gamma - M\alpha$ (*i.e.*, molecular dispersion), must exhibit it also.

The evidence goes to show that both $M\alpha$ and $M\gamma$ are additive, and we conclude therefore that $M\gamma - M\alpha$ must be additive also. However, in the experimental determination of molecular refractivities some error will naturally be made. Now, if the errors made in determining $M\alpha$ and $M\gamma$ for some particular substance are of the same sign they will to some extent (more or less) balance, and a fairly correct value of $M\gamma - M\alpha$ will be obtained; but if these errors are of opposite sign, the sum of the two of them will be borne by the molecular dispersion; and, since the molecular dispersions are always very small numbers, an experimental error of little account when considering molecular refractivities may make itself clearly felt and produce considerable confusion when considering molecular dispersions.

A glance at Table III. shows us that these errors referred to above are not always of the same sign for the same substance; and to this fact is to be traced the irregularity o. the molecular dispersions in question.

We conclude therefore that, although true molecular dispersions can be calculated according to our general method of calculating physico-chemical constants, the examination of the molecular dispersion of a substance gives us a far less reliable criterion of constitution than would be afforded by an examination of its molecular refractivity.

Employing the same general constants for the calculation of molecular dispersions as employed in the calculation of molecular refractivities, and dashing the symbols so as to avoid confusion, the molecular dispersion ($M\gamma - M\alpha$) of the general open chain saturated hydrocarbon—

$$nC + 2(n+1)H + (n-1)L_1$$

is represented by—

$$nA' + (1-n)B'; \text{ but } M\gamma = nA\gamma + (1-n)B\gamma$$

and—

$$M\alpha = nA\alpha + (1-n)B\alpha.$$

This gives the identity—

$$nA' + (1-n)B' \equiv n(A\gamma - A\alpha) + (1-n)(B\gamma \quad B\alpha),$$

whence—

$$A' = A\gamma - A\alpha = 6{\cdot}97 - 6{\cdot}97 = \text{zero},*$$
$$B' = B\gamma - B\alpha = 2{\cdot}27 - 2{\cdot}40 = -0{\cdot}13.$$

Hence, the molecular dispersion of any saturated hydrocarbon can be calculated by multiplying the number of ethane links in it by 0·13. Indeed, we are inclined to consider that 0·13 is the actual influence of the ethane link;

* Heptane is unavoidably omitted from this calculation.

* That is to say, an inappreciably small quantity.

for since it is improbable that the influence of any link or atom on molecular dispersion is negative, it follows from the fact that A′ has an inappreciably small value, that the influences of the carbon and hydrogen atoms and the C.H link respectively are also inappreciably small, since A′ is the sum of the influences due to one carbon atom and four hydrogen atoms and C.H links. Now, $B' = 2H' - L_1'$, so that the above being granted, whence $H' =$ zero (*i.e.*, an inappreciably small quantity), $L_1' = -B' = +0{\cdot}13$. Consequently, the other terms exercising an inappreciably small influence, the molecular dispersion of the general saturated chain hydrocarbon—$nC + 2(n+1)H + (n-1)L_1$—can be written $(n-1)L_1'$. This constant $L_1' = +0{\cdot}13$ is probably the first true *simple* additive constant that has been obtained (see § 1).

Whether we use the formula $nA' + (1-n)B'$ or the above simplification, namely, $(n-1)L_1'$, or calculate molecular dispersions as the differences between the calculated γ- and α-molecular refractivities, the same values will of necessity be obtained. We give both sets of formulæ in Table IV., together with the experimental and calculated molecular dispersions, and the differences between them. The agreement is satisfactory, and compares very favourably with the agreement obtained using Brühl's dispersion constants (see § 7).

(To be continued).

FEHLING'S SOLUTION.

A Contribution to the History of Chemical Reagents.

By B. HERSTEIN.

A history of chemical reagents would form no small and not the least interesting part of the history of chemistry generally, and for obvious reasons. In studying the intramolecular changes of matter chemistry follows strictly inductive methods, taking for granted only the results of direct observation, and while for the purpose of unification we are compelled to classify such results into some comprehensive and consistent system arrived at by logical induction, such hypothetical assumptions are not permitted to influence the direct results of the experiments.

Intramolecular changes of matter, however, are not always directly observable, and to bring them into a condition where our perception would be able to grasp them, we must in the majority of cases resort to what may be described as secondary reactions induced by foreign substances, the so-called chemical reagents. Our processes of differentiation, upon which chemistry in general and analytical chemistry especially ultimately rest, are based upon the behaviour of the various forms of matter towards different chemical reagents, and it follows from this that the progress of chemistry to a very large degree depends upon the introduction of such chemical reagents and an intimate knowledge of their working.

Thus, to quote but one modern instance, it is only necessary to point to the fact that the wonderful insight which we have gained within the last generation into the nature of sugars and carbohydrates generally is due almost exclusively to the introduction of phenylhydrazine as a chemical reagent. Previous to this our knowledge of this group of substances was very limited indeed, and of the few reactions characteristic for this group of substances none was better known than their behaviour towards a solution of copper salts. The reaction upon which the value of this reagent in all its various modifications depends is, as is well known, based upon the reducing effect which certain sugars exert upon such solution, and although analytical chemistry has only within comparatively recent years made use of this reaction, its history runs, nevertheless, far back into the primitive period of human knowledge.

It undoubtedly must first have been observed by the man who introduced the so-called *unguentum Ægyptiacum*—Egyptian ointment—into materia medica, and this probably was none other than an Egyptian priest, if we may draw such conclusions from the name. This *unguentum Ægyptiacum*, which has long since disappeared from all the modern pharmacopœias, but which for long ages was considered a very valuable medicine, forming the basis of various ointments and cosmetical preparations, was prepared by boiling together a mixture of verdigris and honey to which a few drops of vinegar were added. During the boiling the colour of the mass changes considerably owing to the interaction between the glucose and the copper acetate, a change of colour so striking that it could not have escaped notice. Nevertheless, it has never occurred to any of these pharmacists, who in those days were the principal guardians of whatever chemistry there was, to make these changes the independent object of their studies. The first to attempt an explanation of the phenomena observed during this reaction was Antoine Baumé, a celebrated pharmacist of the eighteenth century, who wrote his name indelibly into the history of chemical technology by the device of his spindle. In accordance with the theory then prevailing he said in his "Traité de Pharmacie Théorique et Pratique," that in boiling honey with verdigris and vinegar it is the phlogiston of the acetic acid which, uniting with the verdigris, forms metallic copper, which is deposited. For almost one-half a century this explanation was accepted as satisfactory. During this time, however, the phlogiston theory had been entirely overthrown by Lavoisier, and a period of re-construction had set in, which may be best described by Hegel's phrase "the re-evaluation of all values." Speculative deductions gave place to experimental research, and the balance was made the chief arbiter of the laboratory. A thorough overhauling of all chemical knowledge was undertaken, and in course of time the phenomena observed during the reaction in question were also subjected to renewed scrutiny.

In January, 1815, Dr. Vogel, of Paris, read before the French Academy of Science a paper entitled "A Research Concerning the Decomposition of Salts and Metallic Oxides by Sugars" (abstracted in *Schweigger's Journ.*, 1815, xiii., 162). As indicated by the title, the principal object sought in this investigation was an insight into the mechanism of the reaction, while the products formed during the reaction were studied as closely as the means then permitted, both qualitatively and quantitatively, but only with a view of obtaining light upon the reaction itself. Vogel was able to show that the reddish or brown precipitate which formed on boiling copper acetate with honey and several other sugars then known was not metallic copper, but cuprous oxide, or as it was then called, copper protoxide, that the colour of the precipitate depended very much on the length of time the mixture was heated, and that the precipitation is obtained only from cane, starch, and grape sugar, sugar of milk, also from molasses, manna, and honey, but not from the so-called sweet principle of Scheele. (By this name glycerol, discovered in 1779 by Scheele, was known until well up into the first part of the nineteenth century). Vogel also observed the evolution of carbonic acid gas and acetic acid, which, however, he attributed to the high temperature to which the mixture had been subjected. Using copper sulphate instead of the acetate he claims to have precipitated metallic copper, while copper chloride and copper nitrate, which were likewise tried, seemed not to be influenced at all. Similar observations made almost simultaneously with the preceding were given by J. A. Buchner, Professor of Chemistry in Munich, and published in the succeeding number of the same periodical (*Schweigger's Journ.*, 1815, xiv., 224). On the whole, he merely confirmed the result obtained by Vogel with this exception, that while Vogel had proved the red precipitate to consist of cuprous oxide, Buchner states that during the reaction the sugar is split up, and that one of these cleavage products combines with the copper to form the precipitate.

From time to time other chemists were attracted by the

same subject (Buchholtz, Peschier, Busch; see *Ann. Chem. Pharm.*, 1832, iv., 57). Their work, however, did not materially broaden the problem, which remained one more of theoretical than practical value until the year 1841, when Trommer published his paper, "The Differentiation between Dextrin, Cane, and Grape Sugar" (*Ann. Chem. Pharm.*, 1841, xxxix., 360). Here the subject was approached from an entirely different and more practical point of view. Trommer was able to show that in making the copper salt solution alkaline, it became a valuable reagent for the differentiation between the various sugars and sugar-giving substances. He used an alkaline solution of copper sulphate, and showed that such a solution will yet give a distinctive precipitate of cuprous oxide when boiled with solutions of grape sugar containing only one part in one hundred thousand, and that when the solution of the grape sugar is ten times more dilute, *i.e.*, containing one part to one million, the reaction is yet noticeable in reflected light. The fact that the reaction takes place only in the presence of certain sugars such as glucose, for instance, while cane sugar or dextrin are not acted upon, was fully noticed and made the basis of the differentiation between the different sugars. To Trommer thus belongs the credit of having first introduced the alkaline copper sulphate solution into analytical chemistry, though it was at first used only for qualitative purposes. But the next step was not long in coming, and within a very short time the very same reagent was recommended for use in quantitative chemical analysis.

The estimation of sugars in those days was far from being satisfactory to the chemist engaged in this line of work, depending entirely on two methods. First, the fermentation process devised by Lavoisier and others, and second, the process introduced by Biot, which was based on the deflection of polarised light by sugar solutions. Both methods have their disadvantages, the first requiring considerable time for its completion, quite aside from the fact that the decomposition into alcohol and carbonic acid gas is by no means quantitative, by-products being formed which interfere with the accuracy of the results. The polariscope gives quick and fairly accurate results; requires, however, clear and colourless solutions containing no foreign substances which would deflect the polarised ray. The necessity for an improved method of estimating sugars became so imperious that in 1838 a prize of 3000 francs was offered by the Société d'Encouragement pour l'Industrie Nationale to the chemist who would devise a successful method for the quantitative estimation of sugar. Of the answers received none was acceptable to the committee, and the offer was renewed from year to year until in 1844 Ch. Barreswil submitted his solution (reported in *Journal de Pharmacie*, 1844, [3], vi., 301). The referee of the committee, the well-known Peligot, did not consider the answer entirely satisfactory, but he nevertheless recommended that one-third of the prize, viz., 1000 francs, be awarded to Barreswil for his solution, which, in his opinion (*loc. cit.*), though limited in its application, nevertheless offered a valuable improvement on the existing methods. Barreswil's proposal consisted merely in the extension of the method suggested by Trommer for qualitative differentiation to the quantitative estimation of sugars. The main principle of Trommer's suggestion, *i.e.*, the use of the alkaline copper sulphate solution, was maintained, and the improvement introduced consisted in the addition of a solution of potassium tartrate to prevent the decomposition of the solution on heating. As proposed by Barreswil, the method was a volumetric one, the copper solution being standardised against a pure grape sugar solution of known strength, which latter was added drop by drop to the boiling copper solution, the end-point of the reaction being reached when the blue colour of the solution had disappeared. He also points to the necessity of inverting the cane sugar to glucose, and making two determinations, before and after inversion, where mixtures of the sugars are to be analysed.

The principle of the method was thus established, and its practicability depended very largely upon the stability of the copper solution, which was not very satisfactory. The further efforts of the chemists who studied the subject were therefore directed mainly in this direction, although the use of the method was fully recognised and extended, as by H. Schwartz (*Annalen*, 1849, lxx., 54), who in 1849 proposed it for the estimation of starch, which had previously to be hydrolysed by dilute sulphuric acid to glucose. H. Fehling, by whose name the method is apparently destined to remain known in chemistry, published his first paper concerning the subject in 1848 in a medical publication, and only in 1849 he gave a more detailed account of his work to the chemical fraternity (*Annalen*, 1849, lxxii., 106; 1858, cvi., 75). Fehling's merit consisted chiefly in having worked out with great care the details of the method, giving some account of the stoichiometrical equivalents, but neither did his solution keep for any length of time, nor did he, any more than his predecessors, recognise the fact that the reaction is quantitative only within very narrow restrictions as to the concentration of the solutions and the time of reaction. This point has been established only by the concerted efforts of the many chemists who worked on the subject after Fehling, the necessity for keeping the copper solution divided into two parts being soon recognised. Soxhlet especially devoted much of his time to the study of the method, and established the exact conditions under which the determination must be carried out in order to get satisfactory results (*Zeit. Anal. Chem.*, xviii., 20, 425; for other references to modern investigations see standard text-books).—*Journal of the American Chemical Society*, xxxii., No. 6.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 2nd, 1910.

Prof. Harold B. Dixon, M.A., Ph.D., F.R.S., President, in the Chair.

Messrs. W. P. Bloxam and Hubert L. Lucking were formally admitted Fellows of the Society.

Of the following papers those marked * were read:—

*149. "*The Interaction of Nickel Carbonyl and Carbon Disulphide.*" By Sir James Dewar and Humphrey Owen Jones.

Nickel carbonyl and carbon disulphide vapours interact readily at the ordinary temperature to form carbon monoxide and a bronze-coloured deposit containing nickel, sulphur, and carbon; the liquids, on the other hand, interact only to a very slight extent.

An examination of the volume changes when the two vapours are allowed to react in a specially devised apparatus shows that the reaction is probably represented by the equation (II.) rather than (I.):—

$$2Ni(CO)_4 + CS_2 = 2NiS + 8CO + C \quad . \quad . \quad . \quad (II.)$$

$$Ni(CO)_4 + CS_2 = NiS + 4CO + CS \quad . \quad . \quad . \quad (I.)$$

The reaction, however, is incomplete, proceeds more extensively at low pressures than at higher pressures, and is completely inhibited by the presence of carbon monoxide of a sufficient concentration. Thus, for example, there is no change in a mixture containing nickel carbonyl vapour under 37·5 mm., carbon disulphide vapour under 32·5 mm., and carbon monoxide under 68·5 mm. pressure.

In order to account for the influence of carbon monoxide on the reaction, and for the fact that the reaction, although not reversible, is incomplete, it is suggested that the actual reaction takes place, not between molecules of nickel carbonyl and carbon disulphide, but between free nickel produced by the dissociation of nickel carbonyl and carbon disulphide. The initial concentration of free nickel in the

vapour of nickel carbonyl would be small, and would be much reduced by the presence of carbon moxoxide, to which the dissociation of nickel carbonyl is very sensitive. Consequently, the presence of carbon monoxide would tend to inhibit the reaction until it would finally come to standstill.

DISCUSSION.

The PRESIDENT asked whether it was not *nascent* nickel that reacted with the carbon disulphide vapour. Had the authors observed whether the vapour of nickel carbonyl showed appreciable dissociation throughout its mass when admitted to a vacuous bulb, or whether the discociation only took place in contact with the glass surface?

Dr. JONES replied that the behaviour of nickel carbonyl vapour at low pressures indicated that dissociation takes place in contact with the glass surface, and the interaction with carbon disulphide appeared to take place similarly.

*150. "*Synthesis of Cotarnine.*" By ARTHUR HENRY SALWAY.

The author described in detail an investigation, of which a preliminary account has recently been given (*Proc. Chem. Soc.*, xxvi., 98).

DISCUSSION.

In reply to Dr. Barger, Dr. SALWAY pointed out that the synthesis of cotarnine is complete, since myristicinaldehyde has been prepared by the author from myristicinic acid, which in turn is readily obtained from cotarnic acid (Roser, *Annalen*, 1889, ccliv., 348). The synthesis of cotarnic acid has already been accomplished (Perkin, Robinson, and Thomas, *Trans.*, 1909, xcv., 1977).

*151. "*The Accuracy of the Gold Bullion Assay.*" By JOHN PHELPS.

The author has examined a number of results obtained in the assay of gold bullion from the point of view of the probable error.

The following points were considered:—

1. Gold assays made in the course of routine work in the assay department of the Royal Mint.

2. (*a*) Assays of "trial plates" and comparisons of samples of "proof" gold; (*b*) comparison of proof gold made in the Mint laboratory with that produced by the Utrecht Mint.

3. Comparison of the results of assays made at the Royal Mint with the results of other assayers working on the same material.

4. Discussion on the same lines of results recorded in a paper by F. P. Dewey ("The Assay and Valuation of Gold Bullion," *Trans. Am. Inst. Mining Engineers*, 1909).

The author finds that ordinary gold assays weighed to 0·5 per 1000 are subject to a probable error of $\pm$0·043 per 1000, while in the case of special assays weighed to 0·01 per 1000, the probable error of a single assay may be reduced to $\pm$0·032 per 1000.

From this it is concluded that the error in the mean of twenty assays made with the greatest care should not exceed 0·1 per 1000.

*152. "*Morphological Studies of Benzene Derivatives.*" Part I. Introductory. By HENRY E. ARMSTRONG.

The studies referred to were instituted with the object of ascertaining the general and particular effect of alterations in molecular structure—especially of alterations in the orientation in the molecule of similar radicles—on crystalline form in the case of the extensive series of isomeric tri-derivatives obtained on introducing two like or unlike halogen atoms and the sulphonic radicle in its various forms into benzene. The plan of the work was explained and a general account was given of the course it has taken. The inquiry has been prosecuted in the author's laboratory during the past fifteen years, but the significance of the results arrived at has been apparent only since the development of the Barlowe-Pope theory of the interconnection of external crystalline form and internal molecular structure; the results appear to afford singular confirmation of the theory.

*153. "*Morphological Studies of Benzene Derivatives.* Part II. *Sulphonic Derivatives of the* 1 : 4-*Di-derivatives of Benzene containing Halogens.*" By REGINALD THOMAS COLGATE and ERNEST HARRY RODD.

Twenty-seven compounds of the 1 : 4-series have been measured; the results were fully reported and discussed. The sulphonic chlorides and bromides fall into the one or the other of two crystallographic series; one or two cases of dimorphism have been observed, however, which connect the two series; the connection is further established by the fact that in some cases the sulphonic chloride crystallises in the one series whilst the corresponding bromide crystallises in the other, although, as a rule, there is very close resemblance between corresponding sulphonic chlorides and bromides. The sulphonanilides and the ortho-, meta, and para-toluidides also form an isodimorphous group; in most cases they are obtainable in a labile as well as in a stable form.

It was shown that all the compounds described can be arranged in one or the other of two series, one derived from the hexagonal, the other from the cubic mode of packing equal spheres—the two alternative modes which Barlow and Pope have shown to be possible in the case of benzene units. The results afford most striking evidence of the maintenance of a benzene framework in the molecules.

*154. "*Behaviour of Two Salts with a Common Ion, when Dissolved in an Organic Solvent.*" By JAMES CHARLES PHILIP and HAROLD REUBEN COURTMAN.

The conductivity of solutions of tetraethylammonium iodide and potassium iodide, separately and together, in methyl and ethyl alcohols, methyl ethyl ketone, acetonitrile, and nitromethane has been determined at 25°. The examination of the separate salts has shown that between $v = 50$ and $v = 2000$ the equivalent conductivity is a linear function of the cube root of the concentration; that is, the empirical rule $\lambda = \lambda_\infty - a\sqrt[3]{\eta}$, formulated by Kohlrausch for binary salts in aqueous solution, may be taken as valid also for these salts in organic solvents. On the basis of this rule it is possible by Barmwater's method to calculate the conductivity of a solution containing two salts with a common ion, on the assumption that in the mixture each salt behaves as if it were present alone at a concentration equal to the sum of the concentrations of the two salts. The agreement between the observed and calculated values is such as to suggest that the relation of two salts with a common ion in an ionising organic solvent is closely similar to the relation existing between them when dissolved in water.

DISCUSSION.

Dr. PHILIP, in reply to a question, said that the differences between the observed and calculated values for the conductivity of the mixed iodides were greater than the experimental errors. Formamide had not been tried as a solvent. Like water, it was characterised by a high dissociative power, and for such solvents the differences between the values for the conductivity of the mixed salts calculated by Barmwater's method and those calculated on an additive basis were considerably less than in solvents of weaker ionising power.

155. "*The Effect of Contiguous Unsaturated Groups on Optical Activity.* Part VI. *The Influence of Molecular Symmetry. Application to the Relative Rotatory Powers of Position-isomerides.*" By THOMAS PERCY HILDITCH.

It was shown that, in an optically active compound completely symmetrical with respect to the geometrical centre of its molecule and containing at the same time adjacent unsaturated radicles, there usually exists a very anomalous degree of rotatory power. The direction of the anomaly (positive or negative) is not always the same, and, in particular, negative effects frequently occur when two or more unsaturated groups are in spacial proximity. Similar, but less pronounced, phenomena accompany the presence of partial molecular symmetry coupled with unsaturation.

This effect, together with that due to the conjunction in space of two unsaturated groups (*Trans.*, 1909, xcv., 1577), appears in some measure to explain the deviations frequently observed from Guye's hypothesis (in its simplest qualitative form) in the rotatory powers of optically-active position-isomerides. But utilising derivatives of trisubstituted benzene compounds (such as the phenolic camphor-β-sulphonates) it has been possible to differentiate between the maximum effects due respectively to symmetry (1 : 3 : 5-isomeride) and to the influence of mass ((1 : 3 : 4-isomeride), both of which are concentrated in the para-derivative in disubstituted compounds.

156. "*The Action of Grignard Reagent on Camphoric and* iso-*Camphoric Esters.*" By Yuji Shibata.

The author has recently shown (*Trans.*, 1909, xcv., 1449) that the action of the Grignard reagent on phthalic esters results in the formation of derivatives of phthalide or those of phthalan, whilst glycols are produced from succinic and terephthalic esters, and the conclusion was drawn that the two CO_2R groups in phthalic esters are in the *cis*-position, whilst those in succinic and terephthalic esters are in the *trans*-position. In order to obtain further confirmation of this view, the author has now examined the action of the Grignard reagent on camphoric and *iso*camphoric esters, these being definitely known to be *cis-trans*-isomerides. In accordance with the anticipation, dimethyl camphorate, an ester of the *cis*-acid, gave campholides, whilst dimethyl *iso*camphorate, an ester of the *trans*-acid, gave the non-condensed ester of diphenylhydroxy*iso*camppholic acid. By the action of magnesium *iso*propyl iodide on dimethyl camphorate, a substance, $C_{14}H_{24}O_3$, probably methyl 1 : 2 : 2-trimethyl-3-*iso*butyryl*cyclo*pentane-1-carboxylate, was obtained. The author also discussed the constitution of dimethylcampholide obtained by G. Komppa (*Ber.*, 1908, xli., 1039).

157. "*Some Aromatic Antimony Compounds.*" (Preliminary Note). By Percy May.

By the action of hot fuming nitric acid on triphenylstibine, Michaelis and Reese (*Annalen*, 1886, ccxxxiii., 52) obtained triphenylstibine nitrate, $(C_6H_5)_3Sb(NO_3)_2$, melting at 156°. The author has, however, succeeded in nitrating the benzene nuclei of triphenylstibine, and has obtained a well crystallised *trinitro*-derivative, melting at 191°. This, on reduction with zinc dust and glacial acetic acid, yields the corresponding amino-compound, which can be recognised by the usual tests, but has not yet been isolated in the pure condition. A very small quantity of *tri*-p-*aminophenylstibine* has, however, been obtained by the action of sodium on a solution of antimony trichloride and *p*-chloroaniline in benzene solution. The extreme smallness of the yield is not surprising, as an insoluble compound is formed when a benzene solution of antimony chloride is added to a solution of *p*-chloroaniline in the same solvent, the formation of which tends to prevent the reaction from proceeding. Analysis indicates that this compound is formed by the union of one molecule of antimony chloride with one of chloroaniline. Antimony chloride does not appear to form similar compounds with aniline or with *p*-chlorophenol.

An attempt has been made to sulphonate triphenylstibine, and although it was evident that sulphonation had taken place, no pure compound has, as yet, been isolated from the reaction product.

It is proposed to prepare other substituted derivatives of triphenylstibine by the method indicated above, and also to study the derivatives of the amino-compound.

158. "*Note on the Cobaltinitrites.*" By Mary Cunningham and Frederick Mollwo Perkin.

In a recent paper (*Trans.*, 1909, xcv., 1562), the authors gave a method for the preparation of sodium cobaltinitrite which was found to furnish the best results. Prof. E. Biilmann points out that an almost identical method has been previously described by him. The authors regret that, in searching the literature, the communication of Prof. Biilmann had escaped their attention.

159. "*Acetone Derivatives of* d-*Fructose.*" By James Colquhoun Irvine and Charles Scott Garrett.

The condensation of fructose with acetone gives three fructose-monoacetones, two of which, on continued action, condense with a second molecule of the ketone, giving rise to the α- and β-fructose-diacetones previously described by Fischer. The formation of these three isomerides was explained on stereochemical grounds, and necessitates an extension of the nomenclature of sugar derivatives.

α-Fructosemonoacetone was obtained by the partial hydrolysis of α-fructosediacetone by the action of 0·1 per cent of hydrogen chloride at 30°. Under these conditions only the non-glucosidic acetone residue is removed. The compound melts at 120—121°, and gave $[\alpha]_D$ 20° —158·9° in aqueous solution. *β-Fructosemonoacetone* was obtained as a syrup, and was identified by analysis and by the formation from it of β-fructosediacetone. The third monoacetone compound is incapable of further condensation, and was characterised by conversion into trimethyl fructosemonoacetone (b. p. 120°/15 mm.) by the silver oxide reaction.

The α- and β-fructosediacetones have been further examined. The compounds show a remarkable difference in their behaviour towards hydrolytic agents. In each case the non-glucosidic group is the first to be removed, and this takes place with the α-compound under conditions towards which the β-isomeride is perfectly stable.

160. "*The Absorption Spectra of* 1 : 4-*Dihydronaphthalene and* 1 : 2 : 3 : 4-*Tetrahydronaphthalene.*" By Alfred Godfrey Gordon Leonard.

Bamberger has shown that when reduction is confined to one of the nuclei in the naphthalene molecule, the properties of the compounds so produced are in close agreement with those of analogous benzene derivatives. These substances have been examined to ascertain if there might be any similar relationship between their respective absorption spectra, and the following conclusions are drawn :—

(1) The curves of 1 : 4-dihydronaphthalene and 1 : 2 : 3 : 4-dihyrdonaphthalene are similar, and occupy a position intermediate between the curves of naphthalene and *o*-xylene.

(2) The spectra are those of a benzenoid nucleus as modified by the presence of an aliphatic ring.

(3) Such spectra are in close agreement with the observed chemical properties of the two hydrides.

161. "*The Determination of Malonic Acid by Potassium Permanganate.*" By Alexander Thomas Cameron and Basil Charles McEwan.

In order to extend the observations of Marshall and Cameron on the succinates (*Trans.*, 1907, xci., 1519) to the corresponding malonates, it was necessary to find a conveniently simple method for the quantitative estimation of malonic acid. Durand (*Ann. Chim. Anal.*, 1903, viii., 330) states that malonic acid can be estimated with potassium permanganate in acid solution at 80°, the formic acid, which is one of the products, reacting with the permanganate so slowly that a definite end-point can be obtained. He writes the reaction as :—

$$C_3H_4O_4 + 3O = H_2O + H_2CO_2 + 2CO_2. \quad . \quad . \quad . \quad (1).$$

Concentrated solutions of malonic acid and malonates decompose on boiling, with rapid evolution of carbon dioxide and production of acetic acid. Lamoureux (*Comptes Rendus*, 1899, cxxviii., 998) states that this reaction commences at 68°. Any method requiring a temperature of 80° can evidently only be applied to dilute solutions.

Using Durand's original method, the authors have never obtained a definite end-point ; this is due presumably to the slow but steady oxidation of the formic acid. On the other hand, the truth of the above equation can be easily shown qualitatively. When a dilute solution of malonic acid is distilled with acid permanganate, carbon dioxide is evolved, and the distillate contains formic acid.

An attempt was made to reduce the oxidation of the formic acid to a minimum by heating the malonic acid with excess of permanganate for a few minutes, reducing the permanganate remaining with oxalic acid, and titrating the excess of oxalic acid with more permanganate. According to equation (1), 1 grm. of malonic acid is oxidised by 1·823 grms. of potassium permanganate. In nine titrations the corresponding figure varied from 1·933 to 2·205 grms., showing no regularity.

If complete oxidation of the malonic acid took place, as expressed by the equation :—

$$C_3H_4O_4 + 2O_2 = 2H_2O + 3CO_2 \quad . \quad . \quad . \quad (2),$$

1 grm. of malonic acid would require 2·431 grms. of permanganate. The actual results lie between the two figures, and it is evident that the method is inapplicable owing to the oxidation of an indeterminate amount of formic acid.

Formic acid is immediately oxidised by hot alkaline permanganate, whilst under the same conditions malonic acid is very slowly attacked; hence complete oxidation of the malonic acid can be brought about by first heating with excess of acid permanganate, and then rendering the whole alkaline with excess of alkali.

This method was tested in the following manner :— Either a weighed quantity of solid or (where the weight is given in brackets) a measured volume of standard solution of malonic acid was added to approximately 2N-sulphuric acid, excess of permanganate solution added, and the whole heated to 80–90° for ten minutes (or longer with the more dilute solutions); the solution was then rendered alkaline with strong aqueous potassium or sodium hydroxide, and the heating continued for some minutes; finally, excess of sulphuric acid was added, then for convenience excess of oxalic acid, and this excess determined with more permanganate.

The results are given below :—

No. of experiment.	Weight of malonic acid.	Grms. malonic acid per litre solution.	Grms. $KMnO_4$ per grm. malonic acid.
1.	(0·2004)	2·85	2·382
2.	(0·2000)	1·42	2·431
3.	0·1942	1·30	2·449
4.	(0·2000)	1·25	2·451
5.	0·1850	1·23	2·449
6.	0·1682	1·12	2·419
7.	0·1544	1·03	2·430
8.	(0·2100)	0·66	2 453
9.	(0·2048)	0·43	2·125
10.	(0·2048)	0·40	2·481
	Theory..		2·431

The figures show that the explanation given is the correct one. At the same time they indicate the limits of dilution (calculated on the concentration at the commencement of the reaction) within which the method can be employed quantitatively. In the first experiment some decomposition of the malonate through heat has already taken place, whilst in the last two the results are uncertain. Further experiments on similar lines have indicated that to obtain accurate results it is essential to work below 90° (the reaction commences at about 70°, and proceeds rapidly between 80° and 85°) and to avoid great excess of sulphuric acid.

Mestrezat (*Ann. Chim. Anal.*, 1907, xii., 173) states that tartaric and malic acids react with potassium permanganate in the same manner, with the production of formic acid and carbon dioxide. He suggests a similar method for their estimation.

The case of citric acid (Wöhlk, *Zeit. Anal. Chem.*, 1902, xli., 77) is more complex, but the reaction proceeds on corresponding lines, the chief products being acetone and carbon dioxide.

It is evident that the permanganate reacts with all this series of acids in a parallel manner, and can therefore be used to estimate any one of them only in the proved absence of the others.

(To be continued).

ROYAL SOCIETY.

Ordinary Meeting, June 16th, 1910.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows :—

"*Experimental Researches on Vegetable Assimilation and Respiration. VI. Some Experiments on Assimilation in the Open Air.*" By D. Thoday.

In these experiments Sachs's half-leaf dry-weight method has been employed, with modifications suggested in a previous paper for avoiding errors due to shrinkage of the insolated half-leaves.

Turgid leaves of *Helianthus annuus* were found in bright sunlight to increase in dry weight 17 mgrms. per hour per sq. decim.; thus Sachs's high value is confirmed. Even a slight loss of turgor, however, was accompanied by a diminution in the rate of increase. For this high rate of assimilation a leaf-temperature of 23—24° C. is probably required. It is suggested that Brown and Escombe's low results in bright diffuse light indicate that the stomata of *Helianthus* leaves open to their full extent only in light which is similar in quality to sunlight and approaches it in intensity.

Detached leaves of *Catalpa bignonioides* when fully turgid increased 5 to 6 mgrms. per hour per sq. decim. in bright sunlight; in this plant stomata occur only on the underside of the leaf.

The effect of detachment from the plant upon the rate of assimilation is considered, and evidence is adduced in support of Sachs's assumption in the case of *H. annuus*, that concurrently with assimilation part of the products of photosynthesis are translocated from leaves still attached to the plant.

"*A Case of Sleeping Sickness Studied by Precise Enumerative Methods; Regular Periodical Increase of the Parasites Disclosed.*" By Prof. Ronald Ross, F.R.S., and David Thomson, M.B., B.Ch.

The enumerative methods referred to consist of modes of detecting blood parasites when very scanty, and of counting them accurately. The methods have been applied to a case of sleeping sickness in the clinic of Prof. Ross in Liverpool for seventy-three days continuously, and have shown that the numbers of *T. gambiense* in this patients' blood undergo remarkable periodical variations about every seven to eight days. The authors state that, so far as they can ascertain, though the numbers of trypanosomes had been known previously to vary from time to time, the regular periodicity revealed in their case appears to have been overlooked, possibly owing to insufficient methods of counting. The authors report that numerous parallel researches are being conducted, and give a chart.

"*Recognition of the Individual by Hæmolytic Methods.*" (Preliminary Communication). By Dr. Charles Todd and R. G. White, M.B.

"*Receptors and Afferents of the Third, Fourth, and Sixth Cranial Nerves.*" By Frances M. Tozer, B.Sc., and C. S. Sherrington, F.R.S. (Physiology Laboratory, University of Liverpool).

(*a*) "*Trypanosome Diseases of Domestic Animals in Uganda.*" By Colonel Sir David Bruce, C.B., F.R.S., Army Medical Service; Captains A. E. Hamerton, D.S.O., and H. R. Bateman, Royal Army Medical Corps; and Captain F. P. Mackie, Indian Medical Service. (Sleeping Sickness Commission of the Royal Society, 1908-09).

The commonest trypanosome disease among cattle

Uganda is caused by a trypanosome of the *dimorphon* type, which is probably similar to that sent from the West Coast by Dutton and Todd under the name of *T. dimorphon*, and described by Laveran and Mesnil, and Thomas and Breinl. It seems now that probably Dutton and Todd's *T. dimorphon* is quite different from that which they sent to Liverpool under that name. The original strain of *T. dimorphon* described by them had well-marked di-morphic characters, whereas the trypanosome sent to Liverpool was mono-morphic.

There is some evidence forthcoming that the *T. dimorphon*, as described by Dutton and Todd, really exists, and has been described as occurring in North-West Rhodesia by Montgomery and Kinghorn, and also on the West Coast. Under these circumstances it seems better to give the mono-morphic form, which has up to the present been known by the name of *T. dimorphon*, a new name. It is a small trypanosome, short and stout in form; averaging 13·2 microns in length, with a maximum of 16·0 and a minimum of 10·6. It has no free flagellum, and is restricted in its movements. The conclusions are that :—

1. There is an important trypanosome disease of domestic animals in Uganda.
2. The trypanosome is similar in morphology, action on animals, and cultural characters to *T. dimorphon* as described by Laveran and Mesnil, and to Dr. Edington's trypanosome from Zanzibar, except that this trypanosome is not pathogenic to guinea-pigs.
3. The carrier is unknown, but is probably a *Tabanus*, possibly a *Glossina*, and improbably a *Stomoxys*.

(*b*) "*Experiments to Ascertain if Cattle may act as a Reservoir of the Virus of Sleeping Sickness* (Trypanosoma gambiense).

"*The Lignite of Bovey Tracey*." By Clement Reid, F.R.S., and Eleanor M. Reid, B.Sc.

NOTICES OF BOOKS.

International Language and Science. By L. Couturat, O. Jespersen, R. Lorenz, W. Ostwald, and L. Pfaundler. Translated by F. G. Donnan. London: Constable and Co., Ltd. 1910.

In this outline of the conclusions reached by the International Commission formed in 1900 to investigate the question of an international auxiliary language, different members of the Commission have explained the need for a common language, the principles which must be adopted in its construction, and its relationship to science. The many objections to the idea which have been raised on all sides are skilfully met at the beginning of the book, and if the main contentions of the first chapter are once generally accepted a definite step towards the adoption of the universal language may be the outcome. The members of the Commission have found that Esperanto has much to recommend it, though it is defective in some respects and cumbersome in use, and the language they suggest is based on the same principles and has a certain amount in common with it. The outlines of the grammar of the new language "Ido" are shortly explained, and a very striking tribute to its value is to be found in the appendix, in which a short passage has been translated from English into Ido, and then re-translated by a writer who was unfamiliar with the original; the translated version shows a high degree of accuracy. Anyone who is interested in the establishment of a universal auxiliary language should certainly study this book.

Platinum Resistance Thermometry at High Temperatures. By C. W. Waidner and G. K. Burgess. Washington: Government Printing Office. 1910.

This reprint from the "Bulletin of the Bureau of Standards," vol. vi., No. 2, gives an account of a research in which the use of platinum resistance thermometers was thoroughly investigated. Their advantages and limitations were carefully studied, and the most satisfactory methods of construction and using them were tested. The different types of resistance thermometers are described in the text, and details are given of the calibration of them by observing the resistance in melting ice, steam, and boiling sulphur. Methods of determining melting- and freezing-points of several metals are described, and a summary of the general conclusions to be drawn from the investigation is added. These conclusions relate to the scales employed, to the behaviour of the thermometers in different circumstances, &c., and incidentally some notes on the boiling-point of sulphur are included.

ABC Five-figure Logarithms and Tables for Chemists. By C. J. Woodward, B.Sc. London: E. and F. N. Spon, Ltd.; Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. New York: Spon and Chamberlain. Birmingham: Cornish Brothers. 1910.

This small book of tables will be appreciated by chemists, for it is exceedingly compact, and yet contains most of the data which are to be found in much larger and more pretentious works. Five-figure logarithms are given, with explanations of the methods of using them, and examples of such calculations as the reduction of gas volumes to S.T.P. are worked out. Conversion tables are also included, as well as tables of analytical factors.

Die Gewinnung des Broms in der Kaliindustrie. ("The Production of Bromine in the Potash Industry"). By Dr. phil. Max Mitreiter. Halle-a.-S.: Wilhelm Knapp. 1910.

The growing importance of bromine as a by-product in the potash industry certainly warrants the appearance of this monograph, for information regarding the methods employed, &c., is, generally speaking, difficult to procure, and hitherto has had to be collected from scattered sources. The monograph deals first with chemical methods of preparation, and describes with illustrations the various forms of apparatus which have been employed for the purpose, with their most recent improvements. Electrical methods are next fully treated, and even those processes which have not proved a success commercially are described in detail, their defects and the probable reasons for their failure being pointed out. Methods of purification and analysis and the properties of bromine are also well treated, and the monograph gives a clear summary of the present state of the industry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xliii., No. 6, 1910.

Relations between Constitution and Heat of Combustion of Unsaturated Hydrocarbons.—K. Auwers and W. A. Roth.—Hydrocarbons with conjugated double bonds usually have lower heats of combustion than their non-conjugated isomers, and thus represent structures of less chemical energy or greater saturation. Any factor which has a disturbing influence on a conjugated double bond, as shown by its spectro-chemical behaviour, also affects its thermo-chemical behaviour. Thus the addition of side-chains to the carbon atom of a conjugated system usually raises the heat of combustion of the hydrocarbon; *i.e.*, lowers its degree of saturation. These conclusions have been reached by the study of styrols and terpenes.

Thallo-acetylacetonate.—Edward Kurowski.—Thallo-acetylacetonate separates in small white crystals from an alcoholic solution of acetyl acetone when it is boiled with thallous carbonate. The crystals are quite opaque in transmitted light, and in polarised light show strong interference-coloration. They melt at 160°, undergoing decomposition. The same compound can also be prepared by the action of acetyl acetone on metallic thallium, but this method is not so convenient as the above, because the acetyl acetone is readily decomposed. Carbon disulphide gives a voluminous orange precipitate with an alcoholic or benzene solution of acetone acetate of thalium, and even if traces of carbon disulphide are present in the solution the liquid becomes yellow and turbid.

Perchloric Acid as a Reagent in Organic Chemistry.—K. A. Hofmann, August Metzler, and Kurt Höbold.—Concentrated perchloric acid is a valuable reagent in the study of the basic properties of carbon and oxygen. It may be used to separate carbinols, ketones, and amides from resinous substances, 70 per cent perchloric acid giving pure perchlorates with solutions in ether, benzene, &c. The acid can be split off from the perchlorates merely by the addition of water in the case of weak bases, lime or potassium carbonate being used for strongly basic substances. The authors have prepared and investigated the properties of gallein and cœrulignon perchlorates.

Action of Organo-magnesium Compounds on Boron Trichloride, Sulphur Chloride, and the Chloride and Esters of Sulphurous Acid.—W. Strecker.—When boron trichloride acts on phenyl magnesium bromide only one chlorine atom is replaced by the phenyl residue, and on treatment with water phenyl boric acid is isolated. Phenyl magnesium bromide reacts with sulphur chloride to give phenyl disulphide, $(C_6H_5)_2S_2$, diphenyl being formed as a by-product. With thionyl chloride the corresponding sulphoxide is formed. Symmetrical ethyl sulphite reacts as follows :— $SO(OC_2H_5)_2 + 2MgBrC_6H_5 = 2C_2H_5OMgBr + SO(C_6H_5)_2$, while its isomer gives phenyl ethyl sulphone, $C_6H_5.SO_2.C_2H_5$.

Triphenylmethyl, Triphenylacetaldehyde, and Triphenylacetanhydride. — Julius Schmidlin. — Triphenylacetic acid chloride dissolves in a solution of phenyl magnesium iodide, carbon monoxide being given off.

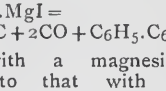
$$2(C_6H_5)_3C.CO.Cl + 2C_6H_5.MgI = 2(C_6H_5)_3C + 2CO + C_6H_5.C_6H_5 + 2MgICl.$$

Thus the reaction with a magnesium organic compound is similar to that with a metal : — $(C_6H_5)_3C.CO.Cl + Ag = (C_6H_5)_3C + CO + AgCl$. The analogous bromide does not behave in the same way, but yields β-benzpinacoline and no carbon monoxide :—

$$(C_6H_5)_3C.CO.Cl + C_6H_5.MgBr = (C_6H_5)_3C.CO.C_6H_5 + MgBrCl.$$

A similar difference in the behaviour of the magnesium organic bromide and iodide has been observed with triphenylchlormethane and β-benzpinacoline. Triphenylacetaldehyde can be prepared from triphenylmethyl magnesium chloride and formic acid ethyl ester. Triphenyl acetanhydride when heated to its melting-point gives off carbon monoxide.

Phospho-monoperacid and Perphosphoric Acid.—Julius Schmidlin and Paul Massini.—By the action of 30 per cent hydrogen peroxide (perhydrol) on phosphorus pentoxide phosphomonoperacid is formed. $P_2O_5 + 2H_2O_2 + H_2O = 2H_3PO_5$. It is a derivative of orthophosphoric acid of formula :—



The acid is more stable in acid than in neutral or alkaline solution. It is a very sensitive reagent for manganese, with traces of which it gives a deep violet coloration when heat is applied. When commercial pyrophosphoric acid is treated with 30 per cent hydrogen peroxide and the mixture is cooled, some perphosphoric acid, $H_4P_2O_8$, is formed. Persulphuric acid anhydride, S_2O_7, can be obtained by the action of ozone on sulphur trioxide.

Vol. xliii., No. 7, 1910.

Lead Peroxide in Elementary Analysis. — M. Dennstedt and F. Hassler.—Although lead peroxide does absorb small amounts of carbon dioxide no appreciable error is introduced into the results of an elementary analysis by its use, provided that large amounts of carbon dioxide are not present and that not more than 10 grms. of the peroxide is employed. It is essential, moreover, to heat the peroxide in the combustion tube to 250—300° for at least half-an-hour before use.

Isomeric Platinum Compounds of Organic Sulphides.—L. Tschugaeff and W. Subbotin.—The compounds of platinum chloride with organic sulphides $PtCl_2 \cdot 2R_2S$ exist in three forms — the α-chloride, $R_2S : Pt<^{R_2S.Cl}_{Cl}$; the β-chloride, $Pt<^{R_2S.Cl}_{R_2S.Cl}$; and the γ-chloride. The authors have now shown that the γ-salt is an analogue of Magnus's salt, and thus platinum compounds with two complex ions exist. Monomeric compounds of the same composition appear to exist only in special cases.

Quantitative Volatilisation of Arsenic.—P. Jannasch and T. Seidel.—Arsenic can be quantitatively volatilised from solutions containing hydrazine sulphate if some potassium bromide or hydrobromic acid is added, the distillation taking an hour at the most. The arsenic can be determined in the distillate either as trisulphide, or as magnesium pyroarsenate, or titrimetrically. The results obtained by this method of separating arsenic from antimony, copper, mercury, and other metals are very accurate, the apparatus required is simple, and the process is rapid.

Phosphorus Pentasulphide. — Alfred Stock. — The author prepared phosphorus pentasulphide by heating red phosphorus with sulphur in the proportions corresponding to the formula P_2S_5. The melting-point of the pure sulphide is 286—288—290° ; the different results obtained being due to the fact that, like the other sulphides, it is partly decomposed when heated. Even at the ordinary temperature decomposition occurs, and preparations which have been kept for some time must be re-crystallised before use. The boiling-point is 513—515° at 760 mm., and the density at 17° is 2·09. The solubility in carbon disulphide is 1 : 450 at room temperature, 1 : 550 at 0°, and 1 : 1200 at −20°. Freshly prepared crystals have hardly any smell ; in the air they gradually produce sulphuretted hydrogen. Water attacks them slowly in the cold, rapidly on heating. In carbon disulphide solution the molecular weight is undoubtedly that corresponding to the formula P_4S_{10}.

Beryllium Formate.—S. Tanatar.—When beryllium carbonate is dissolved in formic acid the normal formate is obtained. It is insoluble in organic solvents. It is more or less hydrolysed by boiling in aqueous solution and is partially decomposed when heated under diminished pressure, a basic salt, $Be_4O(CHO_2)_6$, subliming. The same basic salt is obtained by boiling an aqueous solution of the normal formate with the calculated amount of beryllium carbonate.

MEETINGS FOR THE WEEK.

FRIDAY, 8th.—Physical, 5. "Thermo-electric Balance for the Absolute Measurement of Radiation," by H. L. Callendar. Convection of Heat from a Body Cooled by a Stream of Fluid," by A. Russell. "On Hysteresis Loops and Lissajous' Figures, and on the Energy wasted in a Hysteresis Loop," by S. P. Thompson. "Energy Relations of certain Delectors Used in Wireless Telegraphy," by W. H. Eccles.

THE CHEMICAL NEWS.

Vol. CII., No. 2641.

HALIDES OF TANTALUM.*

By WALTER K. VAN HAAGEN.

The chloride alone of all the possible halides of tantalum has received more than passing attention. A bromide has been recorded, but the iodide is absent from our literature. H. Rose (*Pogg. Ann.*, 1856, xcix., 87) claimed to have obtained the bromide by strongly igniting a mixture of tantalic oxide and carbon in a current of carbon dioxide laden with bromine vapour. He failed to give any analytical results. He surmised that his product was the bromide. Moissan believed it was produced upon heating tantalum metal in a stream of bromine vapour.

With pure materials the conditions essential for the satisfactory preparation of tantalum pentabromide may be briefly summarised:—

1. Tantalic oxide, previously strongly ignited, should be intimately mixed with an excess of pure carbon, an equal weight of the latter being a convenient and quite sufficient amount. Starch carbon answers well, but it usually leaves an appreciable ash, hence pure sugar carbon is preferable. The excess of carbon indicated makes the mass sufficiently permeable to the bromine.

2. Air should be completely expelled. Raise the charge to a full red heat in a current of carbon dioxide to remove the last traces of moisture.

3. Phosphorus pentoxide is essential as the final drying agent for the carbon dioxide.

4. A high temperature must be maintained during the passage of the bromine, otherwise nearly all of it will escape unchanged.

5. The resulting pentabromide should be fused from time to time in order that the combustion tube may not be obstructed.

It is easy to get a yield of about 70 per cent of the theory.

The product from the above procedure was re-sublimed in an atmosphere of carbon dioxide. Upon analysis it showed:—

				Theory.
Ta	= 32·21	32·03	31·79	31·39
Br	= 68·70	68·68	68·38	68·61

Tantalum pentabromide consists of yellow elongated lamellæ, curving or clinging to the tube in beautiful arborescent forms resembling frost flowers. They fuse easily to a transparent ruby-coloured liquid. Their colour is suggestive of that of potassium bichromate. They may be sublimed without melting. The vapour of the bromide is yellow in colour, somewhat resembling that of chlorine. The bromide melts at about 240°, and begins to boil at 320°. It fumes strongly in the air. It dissolves rapidly in absolute methyl or ethyl alcohol, forming at first an amber-yellow coloured liquid which soon becomes colourless. Usually the heat generated causes the alcohol to boil. These reactions certainly point to tantalic esters. Anhydrous ethyl bromide is an interesting solvent for tantalum pentabromide. When the latter is brought into this liquid heat is evolved, and a reddish coloured solution results. If the latter be cooled in water or evaporated in a vacuum desiccator golden-yellow coloured crystals separate. The solution fumes strongly in the air.

Tantalum pentabromide may be sublimed in at atmosphere of hydrogen. This is possible at a temperature just sufficient for the sublimation. At more elevated temperatures a partial reduction to the metallic state occurs. If a lower bromide of tantalum should exist such a compound would not be unlikely to appear at some stage during the reduction of the pentabromide in hydrogen. At first there seemed no evidence of this. At times, however, the sublimate appeared to be different. Indeed, it had been noticed that toward the posterior end of the tube, *i.e.*, beyond the metallic deposit, there was a slight greenish partly almost black film. It dissolved in water with an intense green colour, and in methyl and ethyl alcohol with the same colour. Its analysis indicated a tantalum tribromide, but Chapin, in the John Harrison Laboratory of Chemistry, has since demonstrated that it is not this, but that it is in reality a bromo-tantalum bromide, $(Ta_6Br_{12})Br_2$ (*Journ. Am. Chem. Soc.*, xxxii., 323).

An oxybromide of tantalum was not observed.

Efforts were made both by Rose (*Pogg. Ann.*, 1856, xcix., 593) and by Moissan (*Comptes Rendus*, cxxxiv., 211) to obtain an iodide of tantalum, but without avail. So the query presented itself: is it not possible to transpose tantalum bromide by means of a suitable iodide? Silver iodide suggested itself for this purpose. Accordingly, tantalum pentabromide was distilled through a column of granular well-dried silver iodide in a current of carbon dioxide. A brown sublimate resulted. It contained considerable free iodine, which was carefully expelled, and the residue analysed. This analysis indicated a pentabromide with unmistakable evidences of combined iodine. How could there be free iodine unless there had been a reduction of the bromide?

Finally, it was found that the potassium iodide used in the preparation of the silver iodide contained some iodate. Most likely then the reaction had proceeded as follows:— $7TaBr_5 + 5AgIO_3 = TaI_5 + 3Ta_2O_5 + 5AgBr + 15Br_2$.

The liberated bromine set free iodine from the silver iodide and probably from the tantalum iodide, allowing only a small amount of the latter to escape, while by far the greater portion of the bromide distilled over unchanged. This view is further supported by the fact that iodine separates when tantalum pentabromide is distilled through a layer of potassium iodate.

The next thought was to try hydrogen iodide. Accordingly, tantalum pentabromide was slowly distilled in a steady stream of anhydrous hydriodic acid gas. Soon the reddish colour of the bromide changed to brown, while the escape of hydrobromic acid, together with the excess of the hydriodic acid, could be proved at the exit of the tube. Further, an analysis of the dark brown product showed that only one-third of the bromide had been converted into an iodide. Therefore the experiment was repeated, about 3 grms. of the pentabromide being distilled as slowly as possible in a brisk current of hydrogen iodide for about four hours. The product was brownish black in colour, and showed much iodine. Its tantalum content was found to be 22·98 instead of 22·37 per cent as required by TaI_5. The remainder of the preparation was subjected to another distillation in hydrogen iodide, and analysed with these results:—

Ta (per cent) ..	22·62	22·51
I (per cent)	77·27	77·35

The required percentage of iodine for the pentaiodide is 77·63. These results prove the formation of an iodide, TaI_5. It sublimes in dark nearly black lamellæ, bearing a remote resemblance to iodine crystals. It fuses to a dark brown liquid. Its vapour is like that of bromine. It may be distilled in a current of carbon dioxide without the separation of iodine. It resembles the bromide in its deportment toward moist air and water. An intermediate oxyiodide was never observed.

* An abstract frrom the author's doctorial thesis (1909). From the *Journal of the American Chemical Soci ty*, xxxii.. No. 6.

Royal Institution.—A General Monthly meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. Denys Hague was elected a Member. The Chairman announced that His Majesty the King had graciously consented to become Patron of the Royal Institution.

ON THE CALCULATION OF OPTICO-CHEMICAL CONSTANTS.

Part I.—Aliphatic Hydrocarbons.

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

(Concluded from p. 6).

§ 5. *Molecular Refractivities of Unsaturated Hydrocarbons.* The general formula for open chain ethylene hydrocarbons is—

$$nC+2(n+1-a)H+(n-a-1)L_1+aL_2=$$
$$=nA-(n-a-1)B-a\Gamma,$$

so that knowing the values of A and B, the values of Γ can at once be obtained from the molecular refractivities of such hydrocarbons. Thus, amylene is C_5H_{10}; *i.e.*, $5A-3B-\Gamma$, $M^\alpha = 24{\cdot}65$, $M\gamma = 25{\cdot}45$. Therefore $\Gamma^\alpha = 5A^\alpha - 3B^\alpha - 24{\cdot}65 = 3{\cdot}00$, $\Gamma\gamma = 5A\gamma - 3B\gamma - 25{\cdot}45 = 2{\cdot}59$. Mean values:—$\Gamma^\alpha = 2{\cdot}94$, $\Gamma\gamma = 2{\cdot}62$ (see Table V.).

Using these values, and the values of A and B already obtained, the molecular refractivities (for both $H\alpha$ and $H\gamma$ lines) of all the ethylene hydrocarbons considered have been calculated, and are exhibited, together with the differences between them and the experimental, and the percentage errors in Table V.

It has been found, using the old method of calculation, that in certain compounds (namely, those containing the linking $>C=C-C=C<$) the influence of the unsaturated links is far greater than expected from theory. The consideration of this point we must postpone for the present; it must be understood that the above constants refer only to the simple influence of the ethene links.

With regard to Δ, the data relative to acetylene hydrocarbons is too scanty to allow of the correct value of this constant being thereby obtained; so that we must postpone the calculation of its value until, with the determination of fundamental constants relating to various other groups, we are enabled to employ data relating to substituted acetylenes. The approximate value of Δ can, however, be obtained from the figures given for heptidene. Heptidene is C_7H_{12}; *i.e.*, $7A\ 5B\ \Delta$. $M^\alpha = 32{\cdot}46$, $M\gamma = 33{\cdot}39$. Therefore—

$$\Delta^\alpha = 7A^\alpha - 5B^\alpha - 32{\cdot}46 = 4{\cdot}33;$$
$$\Delta\gamma = 7A\gamma - 5B\gamma - 33{\cdot}39 = 4{\cdot}05.$$

§ 6. *Molecular Dispersions of Unsaturated Hydrocarbons.* The molecular dispersion $(M\gamma - M^\alpha)$ of the general ethene hydrocarbon,—

$$nC+2(n+1-a)H+(n-1-a)L_1+aL_2,$$

is represented by—

$nA'-(n-1-a)B'-a\Gamma'$; but $M\gamma = nA\gamma-(n-a-1)B\gamma-a\Gamma\gamma$ and—

$$M^\alpha = nA^\alpha-(n-a-1)B^\alpha-a\Gamma^\alpha.$$

This gives the identity—

$$nA'-(n-1-a)B'\quad a\Gamma' \equiv n(A\gamma-A^\alpha)-(n-1\quad a)(B\gamma-B^\alpha) - a(\Gamma\gamma-\Gamma^\alpha)$$

whence—

$$\Gamma' = \Gamma\gamma - \Gamma^\alpha = 2{\cdot}62 - 2{\cdot}94 = -0{\cdot}32,$$

and also $A' = A\gamma - A^\alpha$, $B' = B\gamma - B^\alpha$ as before.

In a precisely similar manner it can be shown that $\Delta' = \Delta\gamma - \Delta^\alpha = 4{\cdot}05 - 4{\cdot}33 = -0{\cdot}28$ (approximately).

Hence, the molecular dispersion of any hydrocarbon can be calculated by multiplying the number of ethane links in it by 0·13, the number of ethene links by 0·32, the number of ethine links by a constant approximately equal to 0·28 (exact value to be determined later), and taking the sum of the products thus obtained.

Moreover, if it be admitted that the influence on molecular dispersion of the hydrogen atom and the

Table V.

1. No.	2. Substance.	3. Formula.	4. Formula.	5. M^α found.	6. Γ^α calculated.	7. M^α calculated.	8. Difference between cols. 5 and 7.	9. Error. Per cent.	10. $M\gamma$ found.	11. $\Gamma\gamma$ calculated.	12. $M\gamma$ calculated.	13. Difference between cols. 10 and 12.	14. Error. Per cent.
6.	Amylene	C_5H_{10}	$5A-3B-\Gamma$	24·65	3·00	24·71	+0·06	+0·24	25·45	2·59	25·42	−0·03	−0·12
7.	Hexylene	C_6H_{12}	$6A-4B-\Gamma$	29·34	2·88	29·28	−0·06	−0·20	30·18	2·56	30·12	−0·06	−0·20
8.	Octylene	C_8H_{16}	$8A-6B-\Gamma$	38·55	2·81	38·42	−0·13	−0·34	39·66	2·48	39·52	−0·14	−0·35
9.	Decylene	$C_{10}H_{20}$	$10A-8B-\Gamma$	47·38	3·12	47·56	+0·18	+0·40	48·73	2·81	48·92	+0·19	+0·39
10.	Valerylene	C_5H_8	$5A-2B\ 2\Gamma$	24·16	5·89 × ½	24·17	+0·01	+0·04	24·99	5·32 × ½	25·07	+0·08	+0·32
11.	Diallyl	C_6H_{10}	$6A-3B-2\Gamma$	28·77	5·85 × ½	28·74	−0·03	−0·10	29·78	5·23 × ½	29·77	0·01	0·03

Mean $\Gamma^\alpha = 2{\cdot}94$ Mean $\Gamma^\gamma = 2{\cdot}62$

Table VI.

1. No.	2. Substance.	3. Formulæ.	4. Formulæ.	5. Formulæ.	6. $M\gamma - M^\alpha$ found.	7. $M\gamma - M^\alpha$ calculated.	8. Difference between cols. 6 and 7.
6.	Amyiene.. ..	C_5H_{10}	$5A'-3B'-\Gamma'$	$3L_1'+L_2'$	0·80	0·71	−0·09
7.	Hexylene ..	C_6H_{12}	$6A'-4B'-\Gamma'$	$4L_1'+L_2'$	0·84	0·84	0·00
8.	Octylene.. ..	C_8H_{16}	$8A'-6B'\ \Gamma'$	$6L_1'+L_2'$	1·11	1·10	−0·01
9.	Decylene . ..	$C_{10}H_{20}$	$10A'-8B'\ \Gamma'$	$8L_1'+L_2'$	1·35	1·36	+0·01
10.	Valerylene ..	C_5H_8	$5A'-2B'-2\Gamma'$	$2L_1'+2L_2'$	0·83	0·90	+0·07
11.	Diallyl	C_6H_{10}	$6A'-3B'-2\Gamma'$	$3L_1'+2L_2'$	1·01	1·03	+0·02

Table VIII.

	M^α.	$M\gamma$.	$M\gamma - M^\alpha$.
$C+4H$	$A^\alpha = 6{\cdot}97$	$A^\gamma = 6{\cdot}97$	$A' = 0{\cdot}00$
$2H\ L_1$	$B^\alpha = 2{\cdot}40$	$B^\gamma = 2{\cdot}27$	$B' = -0{\cdot}13$ (or $L_1' = 0{\cdot}13$)
$4H-L_2$	$\Gamma^\alpha = 2{\cdot}94$	$\Gamma^\gamma = 2{\cdot}62$	$\Gamma' = -0{\cdot}32$ (or $L_2' = 0{\cdot}32$)

TABLE VII.

1. No.	2. Substance.	3. Formula.	4. M^{α} Found.	5. M^{α} Calculated Brühl.	6. M^{α} Calculated Redgrove.	7. Difference between cols. 4 and 5.	8. Difference between cols. 4 and 6.	9. $M\gamma$ Found.	10. $M\gamma$ Calculated Brühl.	11. $M\gamma$ Calculated Redgrove.	12. Difference between cols. 9 and 10.	13. Difference between cols. 9 and 11.	14. $M\gamma - M^{\alpha}$ Found.	15. $M\gamma - M^{\alpha}$ Calculated Brühl.	16. $M\gamma - M^{\alpha}$ Calculated Redgrove.	17. Difference between cols. 14 and 15.	18. Difference between cols. 14 and 16.
1.	Pentane . .	C_5H_{12}	25·30	25·06	25·25	− 0·24	− 0·05	25·71	25·69	25·77	− 0·02	+ 0·06	0·41	0·63	0·52	+ 0·22	+ 0·11
2.	Hexane . .	C_6H_{14}	29·70	29·63	29·82	− 0·07	+ 0·12	30·41	30·37	30·47	− 0·04	+ 0·06	0·71	0·74	0·65	+ 0·03	− 0·06
3.	Heptane . .	C_7H_{16}	34·32	34·20	34·39	− 0·12	+ 0·07	—	—	—	—	—	—	—	—	—	—
4.	Octane . .	C_8H_{18}	38·95	38·77	38·96	− 0·18	+ 0·01	39·90	39·73	39·87	− 0·17	− 0·03	0·95	0·96	0·91	+ 0·01	− 0·04
5.	Decane . .	$C_{10}H_{22}$	48·21	47·92	48·10	− 0·29	− 0·11	49·37	49·10	49·27	− 0·27	− 0·10	1·16	1·18	1·17	+ 0·02	+ 0·01
6.	Amylene . .	C_5H_{10}	24·65	24·69	24·71	+ 0·04	+ 0·06										
7.	Hexylene . .	C_6H_{12}	29·34	29·26	29·28	− 0·08	− 0·06										
8.	Octylene . .	C_8H_{16}	38·55	38·40	38·42	− 0·15	− 0·13										
9.	Decylene . .	$C_{10}H_{20}$	47·38	47·55	47·56	+ 0·17	+ 0·18										
10.	Valerylene . .	C_5H_8	24·16	24·32	24·17	+ 0·16	+ 0·01										
11.	Diallyl . .	C_6H_8	28·77	28·89	28·74	+ 0·12	− 0·03										
					Average error =	0·147	0·075				0·125	0·063				0·070	0·055

C.H link is negligible (see § 4), L_2' must equal 0·32, and the value of L_3' can be similarly obtained. In this case, the general formula for open chain ethene hydrocarbons becomes $(n - 1\ a)L_1' + aL_2'$.

Whether we use this formula, or the non-simplified one, or calculate molecular dispersions as the difference between the calculated γ- and α-molecular refractivities, the same values will of necessity be obtained. We give both sets of formulæ in Table VI., together with the experimental and calculated molecular dispersions, and the differences between them. The agreement is very satisfactory.

§ 7. *Criticism of Brühl's Method of Calculating Optico-chemical Constants.*

We have already indicated one error in Brühl's method of calculating optico-chemical constants; namely, that due to the ignoring of the influences of the ethane and certain other links. This very common error we have dealt with in general terms in the opening chapter of our monograph, "On the Calculation of Thermo-chemical Constants," and nothing further need be said on this matter. There is, however, another fundamental error in Brühl's calculations. He bases his constants on the results obtained for aldehydes and ketones, which he treats as if they were true carbonyl-oxygen compounds—otherwise the method adopted would not hold good. But chemists are inclined nowadays to regard such bodies as mixtures (under ordinary conditions) of the two dynamic isomers — the enol and the ketol form—and hence Brühl's calculations are fallacious.

Now, the first of these errors is of such a nature that it is not indicated by a comparison of the theoretical and experimental results, since the same errors are (and must of necessity be) made in applying the constants as are committed in obtaining them; this, however, affords no excuse for employing the method in question. The other error, however, should be indicated by a disagreement between the results obtained experimentally for some simple substances (which were not made the basis of the method of calculation in question) and the calculated values. Evidently the hydrocarbons would constitute such a criterion in question.

In Table VII. we give a comparison of the experimental molecular refractivities and dispersions of the hydrocarbons considered in this paper with the theoretical values calculated according to Brühl,* and according to the method outlined herein, respectively. In using Brühl's constants we have necessarily assumed with Brühl that the value of the C.H and C.C links is zero, so that the values obtained are not affected by this error of Brühl's. Brühl's values for $M\gamma$ have been obtained as the sum of M^{α} and $M\gamma - M^{\alpha}$. The average error for each set of results is obtained by dividing the sum of the individual errors (neglecting signs) by the number of individual errors, and gives a relative criterion of the accuracy of the method of calculation.

With regard to both α- and γ-refractivities the average error in the case of Brühl's theoretical values is almost twice that given by our method. And with regard to molecular dispersions, the average error in the case of Brühl's theoretical values is also greater than that given by our theoretical values. Brühl did not obtain a constant value for the influence of the ethene link on molecular dispersion, so no comparison is given in the case of $M\gamma$ and $M\gamma - M^{\alpha}$ for ethene hydrocarbons.

Table VIII. gives, in a convenient form, the values of the "fundamental optico-chemical constants" obtained in this paper.

ERRATUM.—P. 5, col. 1, line 21 from bottom, *for* "C+2*H* −L_1," *read* "C+2*H*+L_1."

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* Brühl's constants are as follows:—Refractivity constants, C = 2·365, H = 1·103; ethylene bond, = 1·836; dispersion constants, C = 0·039, H = 0·036 (see *Zeit. Phys. Chem.*, 1891, vii., 191).

A COMPARISON OF THE METHODS FOR DEPOSITING IRON ELECTROLYTICALLY.

By S. A. TUCKER and E. SCHRAMM.

THE experiments herein described include the sulphate and chloride baths as these have been used by most investigators. Other electrolytes have been tried without much success, such as ferrous fluorsilicate, but it was considered best to restrict the experiments to the more promising methods and, by comparing them under certain conditions, to decide which would be the most practical for the deposition of metallic iron.

The first solution tried was made by dissolving 200 grms. of $FeSO_4.(NH_4)_2SO_4.6H_2O$ in one litre. This gives about 29 grms. of iron per litre, or a concentration of 2·9 per cent of iron. This is the solution as used by Amberg (*Zeit. Electrochem.*, 1908, xiv., 326), and probably by Burgess (*Trans. Am. Electrochem. Soc.*, 1904, v., 201; *Electrochem. and Met. Ind.*, 1904, ii., 183) and Hambuechen. The cathodes were clean sheet iron, and the anodes consisted of wrought iron bars. The experiments were carried on at room temperature and the results are given in Table I.

TABLE I.—*Iron.*

Volts.	Ampère.	Ampère square dcm.	Ampères square foot.	Lbs. kw.-hour.
0·50	0·2	0·176	1·63	4·4
0·56	0·25	0·22	2·02	3·94
0·58	0·30	0·264	2·45	3·76
0·64	0·35	0·308	2·96	3·44
0·68	0·40	0·352	3·27	3·21
0·70	0·45	0·396	3·68	3·12
0·74	0·50	0·44	4·09	2·95
0·90	0·75	0·66	6·04	2·42
1·10	1·00	0·88	8·26	1·98

The current efficiency was determined by inserting a copper coulombmeter in series, and gave an efficiency of 95·5 per cent.

The last column in this table shows the effect of increased current density on the energy efficiency. The current was changed temporarily to obtain these figures. In computing the figures for lbs. per kw.-hour, the current efficiency was assumed to be the same throughout.

The deposit obtained was silvery white and of a fine crystalline structure. After a while it became badly pitted. The electrolyte kept in condition for a long time; the basic precipitate which formed by oxidation of the air was allowed to collect in the bottom of the vessel. The electrodes were 1½ ins. apart, and the current density at the anode was about double that at the cathodes.

Another run was made with the solution and all conditions kept the same as the above except the current density, which was raised to 1 ampère per sq. dcm. The deposit was crystalline and silvery white like that obtained at lower current densities, but showed a greater tendency to form nodules. The current efficiency was nearly 100 per cent, but the voltage drop was 1·2, giving 1·705 lbs. per kw.-hour.

A third run was made with ferrous ammonium sulphate solution, with the addition of a small quantity of glycerine. The deposit in this case was smoother and more solid.

Ryss (*Zeit. Elektrochem.*, 1906, xii., 697), in his investigations, used a solution containing 200 grms. ferrous ammonium sulphate, 50 grms. $MgSO_4$, and 4 grms. $NaHCO_3$ per litre. Ryss claimed that such a solution gave a smoother and thicker deposit of iron than could be obtained with ordinary ferrous ammonium sulphate.

A trial failed to show any improvement in the character of the deposits using such additions, but it did show that the bath had a much greater tendency to form basic precipitate, and the time in which it could be maintained in good condition was less than that possible with the simple bath.

The next solution tried was one containing 30 grms. $FeSO_4.7H_2O$, 21 grms. $Na_2SO_4.10H_2O$ per 100 cc. as described by Kern (*Trans. Am. Electrochem. Soc.*, 1908, xiii., 103).

A current density of 1 ampère per sq. dcm. was used. The deposit was dark grey and formed large nodules. At the end of fifteen hours the electrolyte was in bad condition owing to the formation of a heavy precipitate.

The net results of the experiments with different sulphate solutions were the conclusion that a solution containing 200 grms. per litre of Mohr's salt was the best as regards character of deposit, permanent good condition of electrolyte, and energy efficiency. Attention was next turned to the electrolysis of chloride solutions. The first solution used contained 100 grms. $FeCl_2.4H_2O$ and 50 grms. NH_4Cl per litre. The cathodes, as before, being of clean sheet iron, and the anodes wrought iron bar. The electrodes were 1½ ins. apart, and the bath maintained at room temperature. The current efficiency as determined by a copper coulombmeter was found to be 96·5 per cent, and the following data was obtained :—

Time of run 21½ hours.
Average current during run = 0·237.
Average voltage during run = 0·42.
Weight of iron actually deposited, 5·14 grms.
Weight of iron theoretically deposited, 5·32 grms.
Current density during run = 0·304 ampères sq. dcm.
No. watt-hours = $0·237 \times 21\frac{1}{2} \times 42 = 2·14$.
1 watt-hour = 2·4 grms. iron.
1 kw.-hour = 5·28 lbs.

The current was varied temporarily to obtain the following readings.

Volt.	Ampère.	Ampère square dcm.	Ampères square foot.	Lbs. kw. hour.
0·40	0·2	0·260	2·42	5·55
0·44	0·25	0·321	2·98	5·05
0·46	0·3	0·385	3·58	4·83
0·54	0·36	0·450	4·18	4·10
0·57	0·40	0·513	4·76	3·89
0·60	0·45	0·577	5·36	3·70
0·60	0·5	0·642	5·97	3·70
0·72	0·75	0·962	8·94	3·08
1·00	1·00	1·280	11·90	2·22

In the next run a solution of double the strength was used, *i.e.*, 200 grms. $FeCl_2.4H_2O$ and 100 grms. NH_4Cl per litre. The other conditions were kept much the same as before, excepting that the length of time of the run was increased :—

Time of run, 141 hours.
Average current during run, 0·323 ampère.
Average voltage during run, 0·67.
Weight of iron actually deposited, 47·145 grms.
Weight of iron theoretically deposited, 47·6 grms.
Current efficiency = 99 per cent.
Current density = 0·56 ampère sq. dcm. = 5·2 ampères square foot.
No. watt-hours = $0·323 \times 141 \times 0·67 = 30·5$
1 watt-hour = 1·55 grms. iron.
1 kw.-hour = 3·4 lbs.

The following readings were taken :—

Volt.	Ampère.	Ampère square dcm.	Ampères square foot.	Lbs. kw.-hour.
0·42	0·2	0·345	3·2	5·42
0·50	0·25	0·432	4·01	4·55
0·64	0·3	0·517	4·08	3·66
0·70	0·35	0·604	5·64	3·26
0·72	0·4	0·69	6·4	3·16
0·82	0·45	0·726	6·75	2·78
0·84	0·5	0·862	8·0	2·71
0·90	0·75	1·29	12·0	2·53
0·98	1·00	1·725	16·0	2·32

A comparison of the two runs given above with the run on ferrous ammonium sulphate solution shows that while the current efficiency is practically the same in both cases,

the energy efficiency at any given current density is much higher for the chloride solutions. Comparing the two chloride solutions, we see that the more concentrated solution gives a higher energy efficiency at any given current density.

The physical character of the deposit from the chloride solution was somewhat different from that deposited from the sulphate solutions, being more crystalline than the latter excepting that to which glycerine had been added.

The next electrolyte tried was the ferrous sodium chloride solutions described by E. F. Kern (*Trans. Am. Electrochem. Soc.*, 1908, xiii., 103). This was made by dissolving 285 grms. $FeCl_2.4H_2O$ and 102 grms. NaCl per litre, giving 8 per cent Fe and 4 per cent Na. The solution may also be made by dissolving iron in the equivalent weight of HCl. The cathode used was thin sheet iron plate 3¾ ins. × 3½ ins. The anodes were bars of wrought iron 3 ins. × 2 ins. × ½ in. The electrolysis was carried on in a beaker placed on an asbestos pad with a hole cut in it, and heated by placing an incandescent lamp underneath. This kept the temperature between 50° and 70° C.

Previous runs having all shown a high current efficiency of over 95 per cent, it was not considered necessary to use a copper coulombmeter in this run. The object of the run was to :—

(1) Compare the voltage required by this process with the others described.

(2) To find the effect of heating the electrolyte on the energy required.

(3) To find the effect of heating on the physical character of the deposit.

(4) To secure a thick deposit in a short time.

The cathode area was 13·15 square inches.

The electrolyte was kept in condition by adding a little HCl to the bath every day to dissolve the basic precipitate which formed. Water was fed to the bath automatically to make up for evaporation.

The following readings were taken : —

Volt.	Ampères.	Temperature °C.	Current density. Ampères square foot.
	Taken at start.		
0·42	1·4	60	15
0·46	1·4	50	15
0·54	1·4	40	15
0·64	1·4	30	15
	Nine days after start.		
0·36	1·8	60	19·3
0·34	1·6	60	11·15
0·32	1·4	60	15·0
0·30	1·2	60	12·85
0·28	1·0	60	10·72
0·26	0·8	60	8·57
0·24	0·6	60	6·43
0·22	0·4	60	42·9
0·20	0·2	60	2·14

The above tables show : that the voltage decreases with increased temperature ; and that the voltage decreases as the run proceeds.

Comparison of this process with the others tried shows the best energy efficiency for the ferrous sodium chloride electrolyte working at 50—70° C.

This bath also gave the best and thickest deposits, the iron being grey and non-crystalline.—*Journal of Industrial and Engineering Chemistry*, ii., No. 6.

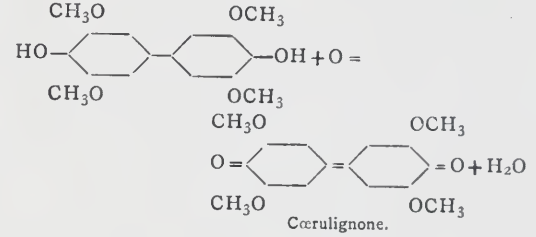
Aloïnose or Sugar of Aloïn.—E. Léger.—Aloïnose is formed by the action of alcohol on barbaloïn at 90°. It has a sweet taste, reduces Fehling's solution, gives the furfurol reaction with aniline acetate, and also G. Bertrand's reaction (violet coloration) with HCl and orcin. $[\alpha_D] = -57·3°$ to $-58·5$. From its reactions it appears o be a pentose.—*Comptes Rendus*, cl., No. 16.

TEST FOR HYDROCYANIC ACID.

By Dr. J. MOIR,
Vice-President of the Chemical, Metallurgical, and Mining Society of South Africa.

AT the meeting of this Society on April 5th at Johannesburg, Dr. Moir demonstrated a new test for hydrocyanic acid of his invention. He said :—"The principle of the test is the oxidising action produced when a cupric salt is added to prussic acid (owing to its reduction to cuprous cyanide). An organic compound which oxidises to a coloured substance is added, and the most sensitive one I have found is hydrocœrulignone. The test is sensitive to something like 1 part in 5,000,000 of water, but unfortunately the reagent is rather unstable'; however, other oxidisable substances of the same class will answer although not so sensitive, and some of these, like benzidine, keep much better. The reactions in the case of the very sensitive reagent (copper acetate, acetic acid, and hydrocœrulignone) are :—

(1) $2Cu\bar{A}_2 + 2HCN + H_2O = 2CuCN + 4H\bar{A} + O.$



Cœrulignone.

In very dilute solutions an instantaneous orange colour is obtained, and in stronger solution a red precipitate of cœrulignone which possesses a violet lustre. If benzidine be used, the colour obtained is indigo blue.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 23rd, 1910.

Mr. A. B. KEMPE, Vice-President and Treasurer, in the Chair.

PAPERS were read as follows : —

"*Damping of Sound by Frothy Liquids.*" By A. MALLOCK, F.R.S.

The object of the note is (1) to explain the well-known fact that a vessel which, when empty or filled with a homogeneous liquid, gives a musical note when struck, ceases to do so when the liquid contains bubbles of gas ; (2) to call attention to the fundamental difference between the damping of waves propagated through a gas containing spheres of liquid (*e.g.*, rain or fog), and that which occurs in a liquid containing bubbles of gas.

The damping of sound waves by fog has received considerable attention, and it has been shown that, although presence of liquid particles does cause a certain amount of dissipation, loss of energy is small, and this agrees with observation.

On the other hand, with a liquid containing bubbles, damping of vibration is excessive, practically the whole of the wave energy being dissipated in a few wave-lengths or periods.

When spheres of liquids are disseminated in a gas, compressions and dilatations take place in the latter much as if only the gas were present, and the increased dissipation is due to slight modification in the motion of the gas, brought about by the liquid spheres.

In the converse case, when bubbles of gas are disseminated through a liquid, variation of volume consequent on the passage of a wave takes place almost entirely in the gas, and distortion of the liquid about the bubbles of whose volume is the variable introduces a rate of dissipation of a different and larger order.

It is pointed out that in a mixture of liquid and gas (in the form of bubbles) the velocity of wave propagation is less than that in either constituent alone, and has a minimum when the proportion of gas to liquid has a certain value. If the mixture consists of air and water, minimum velocity of propagation is reached when the volumes of air and water are nearly equal, and is then about one-fourteenth of the velocity of sound in air.

When the volume ratio of gas to liquid exceeds a certain limit, depending on the order in which the bubbles are arranged, the latter cannot remain spherical, and the mixture then becomes a froth, or collection of air cells separated by thin liquid walls.

It is shown by experiment that such froth is a very effective agent in damping vibrations.

"*Dispersion of Light by Potassium Vapovr.*" By Prof. P. V. BEVAN.

The work described in this paper was an attempt to measure quantitatively the amount of dispersion in the vapour of potassium. Dispersion takes place in the vapour chiefly on account of the red absorption lines, but also to a smaller amount due to other lines of the principal series. Measurements were made showing dispersion affected by the first six pairs of lines of the principal series, and an effect could just be detected at the next pair of lines. The dispersion was found to fit a Sellmeier formula, and values for four of the constants for this formula were obtained.

On theoretical grounds we can conclude, from the relative values of the constants of the dispersion formula that the number of atoms taking part in the absorption of the light after the first pair of lines must be only a small fraction of the total number present in the vapour, and that this fraction decreases with the number of lines in the series. It is suggested that the explanation of series lines must therefore be looked for in systems which are not the atom pure and simple, but probably atoms to which a corpuscle or more than one corpuscle become attached. Several types of quasi compounds may thus be formed in a way suggested by Sir J. J. Thomson, and the periods commonly associated with the atoms may be the periods of these systems. Our conception of the atom may be thus considerably simplified, as the number of degrees of freedom for each individual atom may be diminished very largely if this view be the true one.

"*Additional Refractive Indices of Quartz, Vitreous Silica, Calcite, and Fluorite.*" By J. W. GIFFORD.

"*Absorption Spectra of Sulphur Vapour at different Temperatures and Pressures, and their Relation to the Molecular Complexity of this Element.*" By J. IVON GRAHAM, Royal College of Science for Ireland.

The absorption spectra were photographed at temperatures varying from 530° C. up to 900° C., at atmospheric pressure, and at constant temperatures, under pressures between atmospheric and 10 mm. of mercury. The photographs at constant pressure with the above variation of temperature show the presence of two distinct absorption spectra; these are attributed to the intra-molecular vibrations of the S_8 and S_2 complexes respectively, the former producing a series of absorption bands between $n(=\lambda^{-1})$ 2000 and n 2600, with mean position of maximum absorption about n 2500, whilst the relatively lighter S_2 molecular system, by taking up vibrations of greater frequencies, produces a series of bands lying between n 2900 and n 3820, with mean position of maximum absorption about n 3750.

Since *only two* distinct spectra are evident, it is concluded that the equation $S_8 = 4S_2$ represents the sole reaction that occurs in the dissociation of sulphur vapour on heating from its boiling-point up to 900° C. The interpretation of the photographs of the absorption spectra of the vapour at different (constant) temperatures, but with reduction of pressure, indicates that above 580° C. the dissociation of the molecule S_8 is simple; that is, there is direct dissociation into S_2 complexes, but at or below 520° C. the dissociation takes place with the formation of molecules intermediate in complexity between the above two aggregates.

The position of maximum absorption of each band is towards the more refrangible edge, whilst the individual bands of each series appear to become stronger, also in the more refrangible direction. The two series of bands are shown mapped in oscillation frequencies, the similarity between the series being much more evident when illustrated in this manner.

Reproductions of photographs also accompany the paper.

"*Wave-making Resistance of Ships: a Study of certain Series of Model Experiments.*" By T. H. HAVELOCK, M.A., D.Sc.

In a previous paper (*Proc.*, A, 1909, lxxxii., 276) the author discussed the variation of the wave-making resistance of a ship with its speed, and a formula was obtained by specifying the action of a ship in terms of a simple equivalent pressure distribution travelling over the surface. The present investigation is a more systematic study of some of the coefficients of the formula, the experimental data being taken from published records of tank experiments with models. The discussion is limited to types for which the resistance-velocity curve shows clearly the humps and hollows which are usually ascribed to interference of wave systems originating at the bow and stern; the tabulated results form a numerical study of the latter theory, and exhibit the variation of the coefficients of the simple equivalent pressure system with the displacement of the model, the proportion of parallel middle body, and various coefficients of fineness. Without attempting to express the coefficients by empirical formulæ, sufficient information is available to allow of an approximate estimate of their values in similar models; this is illustrated by the *Turbinia*, and the result is discussed in relation to the published record of trials of that vessel. The characteristic interference effect mentioned above appears to occur specially in rather full-ended models, with fairly high cylindrical coefficients; in this case it is permissible to regard the equivalent pressure system as having two parts associated with the bow and the stern respectively. An examination of models with finer ends suggests that this simple interference theory is inadequate in certain cases; the study of a modified type of pressure distribution is indicated.

"*Blood Volume of Mammals as Determined by Experiments upon Rabbits, Guinea-pigs, and Mice; and its Relationship to the Body Weight and to the Surface Area expressed in a Formula.*" By GEORGES DREYER, M.A., M.D., and WILLIAM RAY, B.Sc. (Oxon.), M.B. (Adelaide).

"*Autotoxæmia and Infection.*" By E. C. HORT, F.R.C.P.Ed.

The object of this communication is to show that fever, loss of weight, and changes in the antitryptic values of the blood serum, three phenomena common to bacterial and protozoan infection in man, can be reproduced in animals by the subcutaneous injection of small quantities of distilled water. Elaborate controls were set up throughout, and absence of sepsis repeatedly proved by autopsy and by microscopical sections.

Fever.—Sixty guinea-pigs received single injections of boiled distilled water in quantities varying from 1 to 10 cc. Fever resulted in fifty. Thirty guinea-pigs received multiple injections, always followed by fever except when the injections were too closely crowded, or too large, when sub-normal temperatures resulted. Twelve rabbits received single injections varying from 10 to 60 cc. Fever followed in all. Ten rabbits received multiple injections. All showed fever. Fever after each injection was always rapid in onset, abrupt and fugitive in both guinea-pig and

rabbit. By appropriate spacing of injections continuous fever can be produced, ceasing with the injections. Hypersensitisation was frequently observed. Establishment of a constant between weight of injection, animal injected, and degree of fever induced has been so far impossible.

Weight.—The effect of small single injections was inconclusive. Multiple injections always produced marked loss, recovery ensuing on discontinuance of injections if few in number.

Antitryptic Values.—Multiple injections produced marked rise in values, strikingly parallel in gross effect to the rise produced in the same species of animal by single injections of diphtheria toxin, or of emulsions of living bacteria.

From these experiments it would appear that, however great the share taken by bacteria and protozoa in initiating the disease-complex of infection, the net result is, perhaps to a large extent, a state of true auto-intoxication.

The results obtained suggest that such auto-intoxication is in part directly due to absorption of derivatives of the infected cells themselves, and only indirectly to the absorption of bacterial products.

CHEMICAL SOCIETY.

Ordinary Meeting, June 2nd, 1910.

Prof. Harold B. Dixon, M.A., Ph.D., F.R.S., President, in the Chair.

(Concluded from p. 10).

162. "*The Direct Union of Carbon and Hydrogen. Synthesis of Methane.*" Part II. By William Arthur Bone and Hubert Frank Coward.

In continuation of their previous experiments (*Trans.*, 1908, xciii., 1975), the authors are now able to report a not less than 95 per cent yield of methane from less than 0·03 grm. of highly purified sugar charcoal (containing not more than 0·06 per cent of ash and less than 0·1 per cent of hydrogen) by maintaining it in a steady current of pure dry hydrogen at 1150° for from seventeen to twenty-five hours continuously, thus completing the proof of the direct synthesis of methane from its elements at this temperature.

163. "*The Existence of Racemic Compounds in Solution.*" By Albert Ernest Dunstan and Ferdinand Bernard Thole.

In continuation of their previous work (*Trans.*, 1908, xciii., 1815) the authors have investigated the viscosity-concentration relationships for various solutions of active and racemic compounds. The *sec.*-octyl hydrogen phthalates (*d*-, *l*-, and inactive forms) were examined in benzene solution, and were found to give identical curves. Hence the inactive ester does not exist in solution as a racemic compound.

The *d*-, *l*-, and *r*-mandelic acids have the same viscosity in aqueous and in pyridine solutions, but when the viscosities were determined in a non-dissociating solvent, such as amyl acetate, a clear difference between the active and inactive forms was apparent.

Adriani (*Zeit. Phys. Chem.*, 1900, xxxiii., 413) has already proved by Roozeboom's method that *r*-mandelic acid exists in the fused state.

In further support of the previous work on the tartaric acids, it was shown that a solution of racemic acid mixed with *d*-tartaric acid has a viscosity different from that of a solution of the pure *d*-acid of identical concentration.

164. "*Note on the Occurrence of Osyritrin (Violaquercitrin) in Osyris abyssinica.*" By Samuel James Manson Auld.

In an examination of "Pruimbast" or "Cape Sumach," *Osyris compressa* (*Colpoon compressum*), A. G. Perkin (*Trans.*, 1897, lxxi., 1132) separated a glucoside, *osyritrin*, which he later showed to be identical with violaquercitrin, isolated previously by Mandelin (*Jahresber*, 1883, 1369) from *Viola tricolor*. Samples of Cape sumach have been examined at the Imperial Institute from time to time, and no difficulty has been experienced in separating the osyritrin from them.

Recently a considerable consignment of the leaves and stalks of *Osyris abyssinica*, Höchst, has been received for examination from the Transvaal. The material as received gave a much deeper coloured extract than Cape sumach, and produced a darker leather of rather poor quality. The aqueous extract, on keeping, deposited a certain amount of solid matter, but this did not appear at all similar to the crystalline deposits previously obtained from *Osyris compressa*. The new material was therefore examined more closely.

The Tannins.—Analysis showed that the leaves contained about 23 per cent of tannin.

The leaves were extracted with water and the extract evaporated to a small bulk, when there separated a quantity of solid matter consisting of colouring principle and the phlobaphen of the tannin. The aqueous solution was fractionally precipitated with lead acetate, and the last fraction washed and decomposed with hydrogen sulphide. After removal of the lead sulphide and the excess of hydrogen sulphide, the solution was evaporated to dryness. It yielded a reddish brown tannin of the catechol series. This tannin is much darker than that previously obtained from *Osyris compressa*, and it also shows more readiness to lose water and form the phlobaphen.

Exraction of the Colouring Matter.—The coarsely-ground leaves were thoroughly extracted in a Soxhlet apparatus with 90 per cent alcohol, and the residue, after removing the spirit, was poured into water. The green mass which separated was filtered off, and, after drying, was extracted separately with light petroleum and alcohol. The alcoholic extract set to a viscid semi-solid mass on concentration. By pouring into excess of boiling water it was possible to separate a large quantity of dark brown insoluble matter of a phlobaphen nature, and on cooling the aqueous solution, a dirty brown solid deposit was obtained, which, after repeated precipitation with water from alcoholic solution, yielded a mass of small crystals. These were purified by several crystallisations from dilute alcohol, and finally from boiling water.

A further quantity of the same substance was obtained by deposition from the main filtrate containing the tannin.

The substance formed small greenish yellow needles, melting at 189—190°, after softening at 185—186° (osyritrin melts at 186°). After being dried at 160°, it gave on analysis :—

C = 53·17, H = 4·51. $C_{27}H_{28}O_{16}$ requires C = 53·28, H = 4·60 per cent.

After being dried at 160° : — Found, H_2O = 7·90. $C_{27}H_{28}O_{16},3H_2O$ requires H_2O = 8·15 per cent.

On hydrolysis with dilute acid the substance gives an insoluble colouring matter and a sugar.

The latter is dextrorotatory, and gives an osazone melting at 204—205°. Estimation of the colouring matter gave $C_{15}H_{10}O_7$ = 45·45. The equation $C_{27}H_{28}O_{16} + 3H_2O = C_{15}H_{10}O_7 + 2C_6H_{12}O_6$ requires $C_{15}H_{10}O_7$ = 45·61 per cent.

The colouring matter has all the properties of quercetin, and the penta-acetyl compound, prepared in the usual manner, melted at 190°, and gave on analysis :—

C = 58·48, H = 3·93. Calc. C = 58·59, H = 3·90 per cent.

The glucoside is therefore identical with osyritrin.

165. "*The Relative Influence of the Ketonic and Ethenoid Linkings on Refractive Power.*" By Ida Smedley.

The molecular refractions of the following unsaturated ketones were determined in chloroform solution :—

	M_α.	M_β.	M_γ.
Benzylideneacetone	48·52	51·33	53·79
Benzylideneacetophenone	70·48	75·30	80·2
Cinnamylideneacetone	64·19	70·76	—
Dibenzylideneacetone	84·04	92·17	—
Cinnamylideneacetophenone ..	87·59	98·17	—
Cinnamylidenebenzylideneacetone.	102·69	—	—
Dicinnamylideneacetone	121·5	—	—

The conclusion is drawn that, placed at one end of a chain of conjugated ethenoid linkings, the ketonic and ethenoid linkings have apparently the same effect in exalting refractive power. When interposed in a chain of ethenoid linkings, the effect of the carbonyl group diminishes the exaltation. Its effect is probably then comparable with that of an ethenoid linking contained in a side-chain.

166. "*The Constitution of the β-Diketones.*" By Ida Smedley.

The evidence from the physical properties of the β-diketones was shown to be in harmony with a hydroxyketonic structure, and it is found unnecessary to assume the existence of the di-enolic form. Dibenzoyldimethylmethane (m. p. 99°) was prepared, and the molecular refractions of the following substances were determined in chloroform solutions.

	M_α.	$M_\beta - M_\alpha$.
Benzoylacetone	50·3	3·2
Dibenzoylmethane	74·6	6·9
Dibenzoylethylmethane	75·0	3·4
Dibenzoyldimethylmethane	76·0	2·3
Ethoxybenzylideneacetophenone .	79·6	5·2
Tetraphenylallene	117·7	6·7
Tetraphenylacetone	115·3	4·0

In the preparation of tetraphenylallene (Vorländer, *Ber.*, 1906, xxxix., 1024), tetraphenylacetone, m. p. 28°, was isolated.

The action of the Grignard reagent on dibenzoylmethane and benzoyldimethylmethane was also studied.

167. "*An Apparatus for the Distillation of Fats and Fatty Acids in the Vacuum of the Cathode Light.*" By (the late) James Campbell Brown.

In the course of an investigation of the constitution of various naturally-occurring fats, it became desirable to subject the fats themselves, and also the acids derived from them, to fractional distillation in a high vacuum, with a view to effecting, if possible, a separation into their constituents.

Distillations in the vacuum of the cathode light have been previously carried out, notably by Krafft (*Ber.*, 1896, xxix., 1316), but it was thought that the apparatus used might be considerably improved, more particularly in the case of the receiver.

A series of experiments was therefore entered upon with this object in view, and the apparatus described below is the outcome. It consists essentially of a desiccator, made with a broad flange, on to which the lid was very carefully ground by means of carborundum powder. Inside the lower portion of the desiccator a circular iron plate was fitted on glass bearings in such a way that it could revolve very freely. The best method of doing this was found to be as follows:—

A cork, or, as was afterwards used, a block of lead carrying a pointed glass rod, was cemented to the bottom of the vessel in an exactly central position. The plate was fitted by means of a cork cemented firmly to it with a glass tube which would pass freely over the rod, and the sealed end of which rested on the point of the latter.

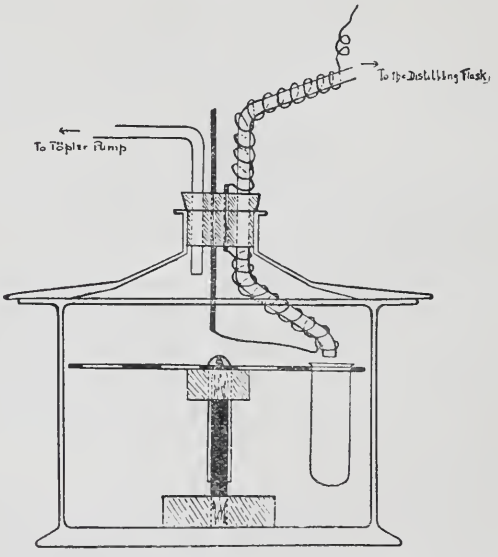
The plate was pierced near its rim with eight holes, each of which carried a test-tube, and each of these tubes could be brought in turn beneath the delivery-tube by means of a magnet worked on the outside of the vessel.

The lid of the desiccator was fitted with a tightly fitting rubber cork, through which passed the delivery-tube and the exit-tube, and also two thick brass rods, the use of which will be explained later. In the earlier experiments this cork was fitted with a mercury tube, but it was found that this was unnecessary, and that the same end could be obtained by lubricating the stopper with a small amount of glycerol. The delivery-tube was sealed to the flask which contained the substance to be distilled, whilst the exit-tube was sealed to a Töpler pump. On the exit-tube was sealed a vacuum tube, through which the passage of an electric discharge was used to determine the vacuum.

On testing the apparatus it was found to hold a vacuum, in which the green fluorescence was visible for at least two hours, and as it was intended to keep the pump at work throughout each experiment, this was considered quite satisfactory.

In the distillation of acids, the melting-point of which was in the neighbourhood of 70°, a difficulty was met with. The acid solidified in the delivery-tube inside the desiccator, and thus brought the distillation to an abrupt close. This difficulty was surmounted by wrapping the delivery-tube with resistance-wire both inside and outside the receiver, and keeping the tube hot by passing a current through the wire. In order to prevent the acid from solidifying in the portion of the tube which passed through the stopper, the tube was heated for about twenty minutes before the experiment was started, and the difficulty was in this way overcome. The brass rods previously mentioned were used to convey the current through the stopper.

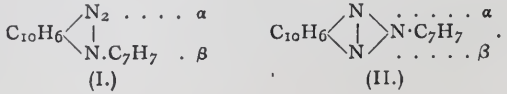
The working of the apparatus will be better understood by reference to the figure, which shows an elevation of



the receiver and a plan of the evolving plate. Many experiments were carried out with it, and in all these it worked extremely well. Its advantages are that it occupies an extremely small space, and that a distillate can readily be divided into any number of fractions, it is very easy to manipulate, while at the same time very high vacua indeed can be maintained in it over a comparatively extended period.

168. "*The* p-*Tolyl*-1 : 2-*Naphthylenediazoimines* (3-p-*Tolyl*-β-*naphtha*isotriazoles)." (Preliminary Note). By G. T. Morgan and Arthur Bramley.

The authors have prepared 2-p-*tolylnaphthylene*-1-*diazo*-2-*imine* (3-p-*tolyl*-β-*naphtha*isotriazole) (I.). m. p. 165—166°, by the action of nitrous acid on 2-*p*-tolyl-1 : 2-naphthylenediamine, and its isomeride, 2-*p*-tolyl-1 : 2-naphthatriazole (II.), m. p. 149°; the latter substance was obtained by oxidising *p*-tolueneazo-β-naphthylamine (m. p. 113°) with chromic acid, and corresponds in properties with the product recently isolated by G. Charrier on heating the foregoing azo-β-naphthylamine at 300° (*Atti R. Accad. Sci. Torino*, 1910, xlv., 131).



The authors propose to examine the physical and chemical properties of other members of the two series of triazenes indicated by the above formulæ.

169. "*A Note on the Aromatic Derivatives of Antimony*." By G. T. Morgan, F. M. G. Micklethwait, and G. S. Whitby.

In pursuing the investigation of certain derivatives of triphenylstibine oxide recently described (*Trans.*, 1910, xcvii., 34), the authors have found that the nitration of triphenylstibine leads to the formation of a *nitro*-derivative, melting at 190°, from which, by reduction, a diazotisable *amine* can be obtained. Some of the acyl derivatives of this base have been prepared.

By the nitration of triphenylstibine hydroxynitrate, a *trinitro*-compound is produced, which on reduction yields a crystallisable *triamine*, furnishing a crystalline *hydrochloride*. This base as also given *acetyl* and *azo-β-naphthol* derivatives, together with *platini-* and *stanni-chlorides*.

The sulphonation of triphenylstibine and triphenylstibine hydroxysulphate has been undertaken, and a soluble *trisulphonic acid* obtained, yielding very soluble alkali salts.

The authors are at present engaged in the further study of these and other derivatives of triphenylstibine.

FARADAY SOCIETY.

Ordinary Meeting, June 21st, 1910.

Dr. F. Mollwo Perkin, Treasurer, in the Chair.

M. Paul Girod sent in a paper entitled "*Studies in the Electro-metallurgy of Ferro-alloys and Steel*," which in the unavoidable absence of the author was read by Mr. F. W. Harbord.

The first portion of the paper describes the various ferro-alloys which are manufactured in Girod furnaces at the works of the Girod Company at Courtepin (3000 h.p.), and, principally at the new works at Ugine (20,000 h.p.), where the furnace electrodes are made.

Ferro-vanadium.—Two varieties are made, one containing 45 to 55 per cent vanadium and 3 to 3·5 per cent carbon, and the other 30 to 40 per cent vanadium with 0·5 to 1·5 per cent carbon. This alloy is employed almost entirely in the manufacture of rapid tool steels with great cutting powers.

Ferro-tungsten.—Three alloys are made, containing respectively 83, 78·5, and 73 per cent tungsten, and 0·6, 1·7, and 3·5 per cent carbon, mostly used for steels to be tempered in air.

Ferro-molybdenum.—This alloy carries 75 to 80 per cent molybdenum and 3 to 4 per cent carbon. The sulphur is removed from the high sulphurous ores in the electric furnace in one operation. Experience has shown that the high carbon content facilitates the fusion, and the mixture of this and the vanadium alloys.

Ferro-chromium.—The principal alloys made contain about 60 per cent chromium and from 0·6 to 9 per cent carbon, with 0·2 to 2·25 per cent silicon.

For the removal of oxygen from fine steels silico-manganese-aluminium and silico-calcium-aluminium alloys are made.

Ferro-silicon.—This is the alloy most largely used, and the varieties made contain 25 to 30, 40 to 75, 75 to 80, and 90 to 95 per cent silicon. The first of these is employed principally in converters, and the richer alloys chiefly for the removal of oxygen and for silicon-steel to be converted into transformer iron.

There are thirty furnaces at Ugine, eighteen utilising 300 to 750 h.p., and nine about 500 h.p.

The Electric Steel Furnace.—The second portion of the paper describes the Girod steel furnace with conducting hearth now in wide use for converting scrap-iron into best quality steels. A feature of the furnace is that the metal conductors have only to be slightly water-cooled, at the parts not in contact with the molten metal, and their life is almost infinite. The large furnaces have a capacity of 15 tons.

The mean content of the charge used at Ugine includes 0·3 to 0·4 per cent carbon, 0·1 to 0·3 silicon, 0·6 to 0·8 manganese, 0·07 to 0·12 sulphur, and 0·07 to 0·12 phosphorus, while the best refined product contains 0·05 to 1·5 per cent carbon, 0·15 to 0·25 silicon, 0·25 to 0·35 manganese, 0·015 sulphur, and 0·015 phosphorus.

The paper concludes with an outline of the two processes, oxidation and reduction, which constitute the refining action of the electric furnace. Tables showing the mechanical qualities of the products are appended.

The Chairman, in opening the discussion, remarked on the comparative backwardness of this country in the adoption of electric steel refining. The question of cheap power in this connection was not so vital as was sometimes supposed.

Dr. W. Rosenhain thought that if the claim that best tool steel could be made from scrap was true, it would revolutionise the Sheffield steel industry. He believed the Sheffield manufacturers were alive to this, and were experimenting in a careful and systematic manner.

Mr. W. R. Cooper also remarked on the fallacy of attaching undue importance to cheap power.

Mr. E. Ristori pointed out that practically all types of electric furnaces in use absorbed about the same amount of energy per ton of steel. England had not taken the lead in this matter of electric refining, and she was not following quickly enough.

Mr. F. W. Harbord, referring to the remarks of the previous speaker, said the value of the results obtained in an electric furnace depended on the facilities present for removing slag carrying the impurities. Recent forms of induction furnaces now made provision for this. He personally had no doubt that steel equal to the best crucible steel could be made from scrap in the electric furnace.

Mr. Ernest F. Law read a paper on "*The Failure of the Light Engineering Alloys, particularly the Aluminium Alloys*."

The paper draws attention to the fact that recent developments in aviation and other branches of modern engineering have created a rapidly increasing demand for suitable light alloys, and that up to the present the metallurgist has not been able to meet this demand satisfactorily. Considering the expectations which were entertained for the aluminium alloys a few years ago, we are forced to the conclusion that in this respect aluminium has been somewhat of a failure.

The constitution of the alloys is then briefly dealt with, and the fact noted that aluminium does not alloy in the true sense of the word with most of the common metals, but combines with them to form brittle metallic compounds. These alloys, during the course of time, spontaneously disintegrate and fall to powder. This fact appears to have been first noticed by the late Sir William Roberts-Austen, and is due to a molecular or allotropic change taking place in the solid alloy. As so many of the alloys undergo this molecular change, it is probably due to an inherent property of the aluminium, and the question is raised as to whether it is possible that aluminium itself exists in two allotropic forms, and that the change from one to the other becomes apparent when the metal is alloyed with another metal.

It is shown that there is evidence in favour of this view, inasmuch as aluminium is known to undergo physical changes during cooling. The evidence is considered briefly, and it is pointed out that, judging by the experience we have gained in the case of the allotropy of iron, if aluminium also proves to be an allotropic metal, then a study of the molecular changes may lead to results of the utmost practical importance.

The Chairman said that metals other than aluminium, such as calcium, manganese, and chromium, disintegrated in the way described in the paper.

Dr. R. Seligman said the lack of cohesion in aluminium below its melting-point existed in the very purest specimens

He therefore questioned whether the phenomena described were due to impurities.

Dr. J. A. HARKER described some experiments he had made on the cooling curve of very pure aluminium. An indication of a kink in the curve appeared at 630° C. (m. p. 657°), but the results were not satisfactory.

Dr. W. ROSENHAIN thought the failure of aluminium alloys was less than the paper would seem to suggest. He described the microscopic changes that he had observed when Al-Mg alloys disintegrated. These polymorphic changes that took place were not confined to metals; they occurred, *e.g.*, in certain silicates of calcium. He believed that allotropic changes in metals depended on the presence of other metals.

Mr. W. H. MERRETT described experiments he had made which confirmed what had been said regarding the anomalous behaviour of aluminium and its alloys. It was interesting that the addition of 5 per cent bismuth greatly facilitated the turning and casting of aluminium.

Dr. T. M. LOWRY said it was remarkable that, unlike other metals, the addition of aluminium and silicon did not harden iron, while it increased its magnetic permeability and decreased its retentivity.

PHYSICAL SOCIETY.

Visit to the National Physical Laboratory.

A NUMBER of special demonstrations had been arranged, of which a brief account is given below.

Dr. HARKER and Mr. EDEN exhibited a vacuum electric furnace in action. The conductor consists of a vertical spiral of Acheson graphite. The current from an alternating supply is led in by massive insulated metal clamps, cooled by a water circulation. For protection against excessive radiation, an insulated screen of a friable quality of carbon is placed round the central conductor. The vacuum-tight casing is a stout casting of gun-metal with conical ends made tight by lead gaskets. Observation windows are provided at each end. The whole, with exception of the windows, is immersed in an outer tank provided with a water circulation. Special attention has been given to the possibility of accurate measurement of the temperatures attained by means of radiation pyrometers. As the furnace had just been completed, and was still giving off gas, the maximum temperature at which it was shown running was only about 1800° C., but much higher temperatures can be reached with ease.

In the mercury thermometer department the various electrically heated baths were shown working.

Mr. CAMPBELL showed a method for the evaluation of self-inductance and absolute determination of the unit of resistance by the help of alternating current. Methods of testing condensers and inductances were also shown working.

Dr. KAYE showed a method of counting the rulings of a diffraction-grating. Along one edge of the grating are ruled a number of short equidistant reference lines at such a distance apart as to include about 100 grating lines. The grating is then mounted on the stage of a projection microscope, and an image (of magnification 1200) of the graduated edge of the grating is thrown upon a screen, which carries a scale of divisions contrived so that the length of each scale division is equal to the distance apart of the lines in the image of the grating. By securing coincidence between the scale and the image, the number of lines between a pair of reference lines can be counted at a glance, and the grating is then racked along by a suitable amount. 1000 lines can be counted in about four minutes.

Dr. ROSENHAIN and Mr. HUMFREY showed their apparatus for observing the behaviour of metals under strain at high temperatures in high vacua. After explaining that one of the principal objects of the research was to observe the effects of plastic strain at high temperatures for the purpose of ascertaining the changes accompanying the allotropic and other transformations which occur in iron and steel at high temperatures, a preliminary apparatus, with which some definite results had already been obtained, was shown. The newer apparatus is practically a small testing-machine giving tensile stresses up to 80 lbs., and provided with a small tubular electric resistance furnace, by means of which the specimen under test can be heated to any desired degree. The whole apparatus is designed to work under a bell-jar, and the joints are arranged so as to be entirely sealed with mercury, the electric furnace leads being brought in through barometer tubes. The testing-machine itself consists of an iron float which can be raised by the admission of mercury to an outer chamber. The stress and strain can both be read off on a steel scale attached to the float, the position of this scale being read against a fixed mark and also against the level of the mercury. The working of the apparatus was demonstrated by stretching in it an india-rubber ring instead of the hot steel strip.

Dr. ROSENHAIN and Mr. CUNNINGHAM showed their apparatus for determining the volume-changes which occur at the melting and freezing of metals and alloys. The method employed is to weigh a small cup full of the alloy or metal under test against a cup containing a copper cylinder, both being immersed in a bath of hot liquid. The suspending wires of the cups also serve as thermo-couple wires so that the temperature of both samples of metal is accurately measured. Specimen curves of results obtained were shown, and the result was indicated that in the lead-tin alloys the eutectic alloy showed the largest contraction on freezing. In connection with this apparatus a new form of portable potentiometer was shown (recently designed and constructed at the Laboratory), in which the E.M.F. of the thermo-couple is determined by partially balancing it by a potentiometer and reading off the remainder by the (small) deflection of a single-pivot galvanometer.

Dr. STANTON and Mr. BAIRSTOW described the apparatus which has been installed for research in aeronautics. The whirling table and dynamometer designed for experiments on propellers were shown in operation, and the methods adopted for obtaining simultaneous measurements of speed, torque, and thrust explained. The dynamometer and propeller are placed at the end of the whirling arm, 30 feet from the centre, and by rotating the arm, the velocity of translation of the propeller through the air can be varied from ten to forty miles per hour.

Wind Channel.—In this apparatus arrangements have been made for measuring the wind resistance of models, the model being held in a fixed position in a current of air. The measuring apparatus has been specially designed to facilitate simultaneous measurements of the "lift" and "drift."

Mr. PATERSON described the work in progress with a view to the reproduction of the unit of candle-power in light of whiter tint than that yielded by the existing flame standards. This is required in the photometry of metallic filament lamps. Various kinds of sub-standards were shown, both carbon and metallic, and the results of tests on tungsten sub-standards described.

Messrs. PATERSON and RAYNER gave some particulars of the work in progress for the Engineering Standards Committee on the ageing and weakening of dielectrics and the measurement of dielectric losses at high voltages.

The arrangements for an investigation undertaken for the Wiring Rules Committee of the Institution of Electrical Engineers, to determine the temperature rise, with normal and other current densities, of cables with various types of covering, were shown by Mr. MELSOM. The tests actually in progress were of 7/16 cables, one cable being drawn into iron tubing and embedded in plaster, and another drawn into iron tubing without any further covering. The temperature of the cable is determined by measuring the

change in resistance of the conductor by a Kelvin Double Bridge.

Arrangements were also shown for determining the insulation resistance of the cable and the temperature coefficient of the conductor.

In addition to the special demonstrations arranged, all the departments of the Laboratory were open for inspection, and the work in progress was described by the assistants in charge of the several divisions.

CORRESPONDENCE.

IRON AND STEEL ANALYSIS.

To the Editor of the Chemical News.

Sir,—While engaged in iron and steel work I found that if a little potassium chlorate, $KClO_3$, is added to the double chloride solution, the steel dissolves much more readily and completely than it does with the solution most generally used.

The solution I use is made up in the following proportions :—

Copper and potassium chloride ..	560 grms.
Potassium chlorate	5 grms.
Hydrochloric acid	250 cc.
Distilled water	1600 cc.

Using about 250 cc. of this solution, a 2·73 grm. sample of a steel containing 1 per cent carbon will, with constant stirring, be dissolved and ready to filter in fifteen minutes at most.

The chlorine and euchlorine set free by the action of the HCl and the $KClO_3$ on each other are, to my mind, responsible for the increased speed of solution.—I am, &c.,

Jerome F. Kohout.

1332, Independence Boulevard, Chicago, Ill., U.S.A., June 22, 1910.

NOTICES OF BOOKS.

Solid Bitumens. By S. F. Peckham, A.M. New York and Chicago: The Myron C. Clark Publishing Co. London E. and F. N. Spon, Ltd. 1909.

The author of this book shows a considerable acquaintance with the work of other writers on bitumens, and has made a somewhat undue use of copious quotations from their publications. On the other hand, he has a good deal to say about his own investigations, and the book gives useful information relating to the advantages of many different methods of proximate, ultimate, and technical analysis of solid bitumens. It is divided into four parts. The first treats of the natural history of the bitumens, discusses their geological occurrence and origin, and gives an outline of methods of classification. Part II. deals with the chemistry of the bitumens, and contains a translation of the whole of Boussingault's Memoir upon their composition. Methods of analysis are criticised in this section, and miscellaneous processes used in the examination of street mixtures, paving blocks, &c., are described. The physical properties of the bitumens and their determination is the subject of the third section, and the book concludes with a short survey of the technology of bituminous streets, in which the advantages and disadvantages of various methods of construction are carefully weighed, and the author states his conclusions as to the necessary conditions to be observed in order to obtain a really satisfactory surface which will wear well.

Radio-chemistry. By A. T. Cameron, M.A., B.Sc. London: J. M. Dent and Sons, Ltd. 1910.

This short handbook on radio-chemistry is based upon a series of articles which the author wrote for *Science Progress* in 1908. These articles have been cast into rather a different shape, and at the same time a good deal of fresh material has been incorporated in them. Much attention is paid to methods of research and to experimental details, the treatment being entirely from a chemical point of view. The transmutation of the elements is the subject of one chapter, in which the author states very fairly the evidence which has been accumulated on both sides, and chemical evidences of the transformation of the elements are also discussed. Although the book is a good introduction to the study of more advanced works it is more than a mere summary of larger text-books, for the author's own ingenious theories are briefly indicated, and he has some interesting observations to make with regard to possible explanations of results which have recently being obtained. The book would make a useful and attractive addition to the library of the fairly advanced student of chemistry who wishes to keep abreast of the times, and it is embellished by the portraits of three workers who have done much to further our knowledge of radio-chemistry—Mdme. Curie, Sir William Ramsay, and Prof. Ernest Rutherford.

The Great Eastern Railway Company's Tourist Guide to the Continent. Edited by Percy Lindley. London: 30, Fleet Street, and 12A, Regent Street. 1910.

This is a well-illustrated and handy little guide to the Continent, in which some tours rather out of the beaten track are briefly described. The information given is probably quite as full as the average traveller requires, and the guide contains some useful maps, and also a vocabulary in English, French, and German of such words and phrases as are likely to be wanted.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cl., No. 16, April 18, 1910.

Internal Friction of Metals at Low Temperatures.—C. E. Guye and H. Schapper.—The authors have studied the internal friction of metals at low temperatures, adopting the method and apparatus of Guye and Freedericksz. They find that copper and zinc have coefficients of friction which decrease, like those of silver, aluminium, and iron. The coefficient of friction of gold rises at the temperature of liquid air. Nickel, palladium, and platinum (the least fusible metals) have such low coefficients that no law of variation of the coefficient with the temperature can be deduced from them.

Ionisation of Liquids.—L. Bloch.—When liquids are separated into very small droplets ionisation is frequently produced, the currents being of the same order of magnitude for the ions of both signs. The liquids investigated could be divided into two classes; the first included distilled water, dilute hydrochloric acid, concentrated caustic potash, normal copper sulphate, ethyl alcohol, amyl alcohol, and acetone, all of which were ionised, while those of the second class, including benzene, essence of terebenthene, mineral essence, olive oil, and vaseline oil, were not ionised. Thus only those liquids which are ionised by bubbling gases through them are ionised when separated into droplets.

Alkaloid of Pseudocinchona Africana. Saponification by Alkalis.—E. Fourneau.—The alkaloid which the author has isolated from *Pseudocinchona* has the composition represented by the formula $C_{21}H_{26}N_2O_3$, and is closely allied to yohimbine, from which, however, it differs in its rotatory power. When the alkaloid is saponified by

means of alkalis it yields an acid of the same composition as that obtained from yohimbine.

Constitution of Dithionates and Sulphites.—H. Baubigny.—Dithionic acid is a disulphonic acid, which may be regarded as the disulphonic derivative of hydrogen, while sulphurous acid which has the asymmetrical formula HSO_2OH in its salts is the corresponding monosulphonic derivative. Thus—

$$\begin{array}{ccc} H & SO_3H & SO_3H \\ | & | & | \\ H & H & SO_3H. \end{array}$$

Hyposulphurous acid is the sulphonic acid of sulphuretted hydrogen, and phenyl sulphurous acid of phenyl hydride.

Constitution of Alcohols obtained by Condensing Secondary Alcohols with their Sodium Derivatives.—Marcel Guerbet.—When the secondary alcohols are heated to about 200° with their sodium derivatives they yield condensed alcohols, the general equation being—

$$C_mH_{2m+1}OH + C_nH_{2n+1}ONa = = C_{(m+n)}\ {}_{2(m+n)+1}OH + NaOH.$$

From the study of the constitution of dicaprylic and secondary tributylic alcohol it appears that the conclusions which have been drawn from di-isopropylic, tri-isopropylic, and secondary dibutylic alcohols may be generalised. The formation of all these condensed alcohols may be ascribed to the elimination of a molecule of water from the OH of one of the alcohols and the hydrogen of the methyl of the other molecule—

$$R—CHOH—CH_3 + CH_3—CHOH—R' = = RCH(CH_3)—CH_2—CHOH—R' + H_2O.$$

When the reaction occurs between two different secondary alcohols the elimination of water takes place at the expense of the hydroxyl of the alcohol which is richest in carbon.

Action of Silver Oxide on Elaterine.—A. Berg.—Silver oxide acts both like an oxidising and a hydrating agent on elaterine, the chief product being elateridoquinone (50–60 per cent of the elaterine employed). A small amount of a phenolic substance (possibly elateridine) is also produced together with an acid which appears to bear to elateric acid the same relation as elateridoquinone to elateridine. A similar, if not identical, acid is produced by the action of alcoholic soda or potash on elateridoquinone.

Cyclohexanetriols and Derivatives.—Léon Brunel.—By the action of iodine and mercuric oxide in presence of water on the ethyl ether of Δ_2-cyclohexanol an oily liquid of formula $C_2H_5O—C_6H_9—(OH)I$ is obtained. On saponification it gives a mixture of two isomeric 1 : 2 : 3-cyclohexanetriols. The two triols cannot be separated by fractional crystallisation in the usual solvents, but the separation can be effected very easily by transforming them into benzoic or acetic ethers.

No. 17, April 25, 1910.

Study of the Constituents of Cocoa-nut Butter. Composition of Essence of Cocoa-nut.—A. Haller and A. Lassieur.—Crude cocoa-nut butter owes its peculiar odour to an essence of which the two principal constituents are methyl ketone and methylnonyl ketone. The butter retains traces of these ketones even after careful purification, and they may be detected by their odour when the butter is heated. The essence also contains small quantities of an aldehyde which has not been isolated. It causes rotation of the plane of polarisation. Essence of rue (*Ruta graveolens*) contains the same ketones. When methylnonyl ketone is hydrogenated in presence of reduced nickel at 250—300° it is partially transformed into a hydrocarbon, C_9H_{20}, which is less rich in carbon than the original ketone, and a pinacoline, $C_{22}H_{44}O$. This is, to the authors' knowledge, the first case of the formation in similar conditions of a pinacoline of such high molecular weight.

Ethyl Ether of Allylcarbinol.—M. Pariselle.—By the action of allyl magnesium bromide on ethyl chlormethyl oxide, $C_2H_5OCH_2Cl$, the ethyl ether, $CH_2=CH—CH_2—CH_2OC_2H_5$, can be obtained. Its boiling-point = 90°; d_0 = 0·811; n_D 17° = 1·396. With bromine this ether gives the dibrom compound $CH_2Br.CHBr.CH_2.CH_2OC_2H_5$, which on saponification yields $CH_2OH.CHOH.CH_2.CH_2OC_2H_5$, and oxyhydrofurfuran, $CH_2—CHOH—CH_2—CH_2$ (with O bridging the last two). With hypochlorous acid the chief product is $CH_2Cl.CHOH.CH_2.CH_2OC_2H_5$, while some $CH_2OH.CHCl.CH_2.CH_2OC_2H_5$ is also formed.

Action of Organo-magnesium Derivatives on Trialkylacetophenones.—Pauline Lucas.—Methyl magnesium iodide with trimethylacetophenone gives a yield of 96 per cent of methylpseudobutylphenyl carbinol. Phenyl magnesium bromide in the same circumstances gives diphenylpseudobutyl carbinol. Propyl magnesium iodide acts like a reducing agent on trimethylacetophenone, giving pseudobutylphenyl carbinol.

Essence of Sea Samphire.—Marcel Delépine.—Essence of sea samphire (*Crithmum maritimum*) contains *d*-pinene, paracymene, dipentene, methyl thymol, and anethapiol. In addition there are present small quantities of other products which go over with the methyl thymol, and which cannot be identified unless very large quantities of the essence are used for the analysis.

Chloroplatinates and Periodides of Di- and Trimethylamine.—J. Bertheaume.—Bresler's method of separating di- and trimethylamine rests upon the insolubility of the chloroplatinate of the former and the solubility of the same salt of the latter in alcohol. The difference of solubility is, however, very small, and varies with the dilution of the alcohol. Hence this method is not very satisfactory. Weiss proposed to separate the two bases by precipitating their hydrochloric acid solution with iodine, and treating the crystalline mass with cold soda solution. The iodide of dimethylamine is, however, an unstable and ill-defined compound, and the method is not exact. It seems not improbable that a method based upon the different degrees of solubility of the periodides of the bases will prove of use for analytical purposes.

MISCELLANEOUS.

Albert Medal of the Royal Society of Arts.—The Society's Albert Medal, which was instituted in 1862 as a memorial of H.R.H. the Prince Consort, and which is conferred annually for "distinguished merit in promoting Arts, Manufactures, or Commerce," has this year been awarded by the Council to Madame Curie for the Discovery of Radium. The discovery, which was the outcome of Prof. Becquerel's researches into the radio-activity of uranium and its compounds, was made jointly by Madame Curie and her husband, Prof. Curie, Professor of Physics at the Sorbonne in 1898. Prof. Curie died in April, 1906, and in May of the same year the Minister of Education, on the recommendation of the Governing Board of the University of Paris, paid his widow the distinguished honour of appointing her as his suocessor. She has since continued, on her own account, the researches she commenced in association with her husband. The Davy Medal of the Royal Society was awarded to Professor and Madame Curie in 1903, and the importance of the discovery has been fully recognised by the scientific world. Madame Curie is the second woman to receive the Society's Albert Medal, it having been conferred, in 1887, on H.M. Queen Victoria "in commemoration of the progress of Arts, Manufactures, and Commerce throughout the Empire during the fifty years of her reign."

THE CHEMICAL NEWS.

Vol. CII., No. 2642.

THE INFLUENCE OF CHLORINE UPON THE DETERMINATION OF NITRIC NITROGEN.

By ROBERT STEWART snd J. E. GREAVES.

It is known that chlorine has an appreciable effect upon the determination of nitric nitrogen by the phenyldisulphonic acid method. Very little information, however, is available as to the amount of chlorine which may be present and not affect the reliability of the results. In connection with the study of the influence of irrigating water upon the movement and production of nitric nitrogen in the soil, this question was investigated quite thoroughly in this laboratory (Utah Experiment Station, *Bull.*, cvi., 80). The results are of interest to others working along similar lines, and also to chemists who are working with problems in sanitary water supply.

The chlorine in the soil under consideration was determined as follows:—An aliquot portion of the extract of the soil, prepared as for the nitric nitrogen determination, was titrated against a one-hundredth normal silver nitrate solution. The results obtained are given in Table I. The results are expressed as parts of chlorine per million parts of soil.

These results indicate quite clearly that the chlorine in the soil under consideration did not exceed 1·134 parts per million.

It was then necessary to determine whether this amount of chlorine would interfere with the determination of nitric nitrogen by the phenyldisulphonic acid method. With this object in view, varying amounts of sodium chloride were added to given quantities of the standard potassium nitrate solution. The nitric nitrogen was then determined in the usual way. The results are very interesting, and will be found in Table II. The results are expressed as parts per million.

Similar determinations were made until a concentration of thirty parts per million of chlorine was reached. No further decrease in the amount of nitric nitrogen found was obtained; *i.e.*, the amount of nitric nitrogen found tended to approach a constant value of nine-tenths of the amount actually present.

The results show that chlorine, when present in quantities as low as 2·638 parts per million, affects the results for nitric nitrogen obtained by this method, less nitric nitrogen being found than is really present.—*Journal of the American Chemical Society*, xxxii., No. 6.

Table I.—*Amount of Chlorine present in the Soil Extract.*

Depth of soil in feet.	Plot No. 41 G.	Plot No. 42 G.	Plot No. 43 G.
1	0·849	0·886	0·780
2	0·814	0·779	0·425
3	0·496	0·697	0·921
4	0·923	0·838	0·709
5	0·567	0·795	1·134
6	0·779	0·602	0·496
7	0·744	0·567	0·922
8	0·673	0·602	0·496
9	0·815	0·673	0·425
10	0·496	0·496	0·425

Table II.—*The Effect of Chlorine on the Sensitiveness of the Method.*

Chlorine added.	Nitric nitrogen present.	Nitric nitrogen found.
0·5278	0·1	0·1
1·056	0·1	0·1
1·584	0·1	0·1
2·113	0·1	0·1
2·638	0·1	0·095
3·167	0·1	0·090
3 694	0·1	0·098
4·224	0·1	0·090
4·749	0·1	0·090
5·278	0·1	0·1
5·886	0·1	0·095
6·342	0·1	0·094
6·856	0·1	0·092
7·362	0·1	0·092
7·917	0·1	0·092
8·446	0·1	0·092
8·9776	0·1	0·090
9·496	0·1	0·086

THE DETERMINATION OF OXIDES OF IRON AND ALUMINA IN FLORIDA PHOSPHATES.

By H. HERZOG.

The method as given below is a modification of the old Glaser method, and can be depended upon to give excellent results in all except the few instances in which manganese occurs in any appreciable quantity. It must also be noted that this method does not include any iron or alumina present in the shape of pyrite, or as a silicate insoluble in acid. With reasonable care in the various operations, the results on the identical pulverised sample should not differ more than 0·05 per cent, and are generally well within this limit. The most important points appear to be the proper elimination of fluorine, and the use of *very hot* water in washing the precipitate. As carried out in this laboratory, the operations are as follows:—

One grm. of the powdered sample is carefully weighed out and placed in a tall beaker of about 300 cc. capacity. Ten cc. of strong muriatic acid are added, and after covering with a watch-glass, the beaker is placed on a gauze and quickly brought to a boil. Leave on the gauze for ten minutes, regulating the flame so that it does not go dry, and the bulk of the solution at the end of the ten minutes is about 5 - 7 cc. Let cool, and carefully decant as completely as possible into a Jena glass volumetric flask of 100 cc. capacity. Try to get all the solution to run into the flask, excepting the last drop or so. Rinse this last drop into the flask with the least possible amount of water. It is possible to do this with a little practice, without disturbing the bulk of the sand, which remains (most of it) in the original beaker. You now have about 10—12 cc. solution in the little volumetric flask. To this solution in the flask you add 10 cc. of dilute sulphuric acid (one-half acid of 1·84 sp. gr. and half water).

The addition of this acid will form a curdy, bulky precipitate of impure sulphate of lime. Shake up the flask to mix this precipitate, and then place the flask on a gauze over Bunsen in the hood, and boil for at least ten minutes.

It may require a little practice to get the flame just right, to get the flask and contents to boil hard without bumping off the stand—but it is most important that the contents should boil. This boiling gets rid of nearly all the fluorine, and changes the bulky precipitate of calcium sulphate into a dense crystalline compound, which filters and washes easily. My experience has been that a gauze and Bunsen are better than hot plate or sand-bath for this particular operation, as a quick heat gets the solution to a temperature where the violent pumping (caused by the occasional liberation of a large bubble of vapour) is avoided by causing the evolution of steam, &c., to be so rapid as to form a more continuous stream.

After ten minutes' boiling, take the flask off the fire and let cool to room temperature.

To go back to the beaker in which the original solution was made, it is possible that the grains of sand and insoluble matter might not have been rinsed quite clean in transferring to the flask. It is therefore the practice to

add to this residue a few cc. of alcohol (95 per cent). These alcoholic rinsings are now added to the cooled flask containing the dense calcium sulphate, and the solution made up to the mark with alcohol and allowed to stand at least one hour. (It will not hurt to stand over night).

There is some shrinkage in this alcoholic solution, which must be made up to the mark with more alcohol.

After standing the solution is filtered on a dry filter into a dry beaker, or into a dry porcelain evaporating dish of about 5 inches diameter, if all the solution is to be used.

In case the flask is graduated to allow for the bulk occupied by the calcium sulphate precipitate, the dry beaker is used to catch the filtrate—and an aliquot portion of 75 cc. is withdrawn with a pipette, and this aliquot (corresponding to ¾ grm.) is used for the further tests. If you have not allowed for the bulk of the precipitate, it will be necessary to filter *all* the solution from the flask, and wash it with alcohol until free from foreign matter.

Assuming that you have withdrawn 75 cc. for analysis, place this in the 5-inch evaporating dish, and then place the dish in a pan containing about one-half inch in depth of water. This water is used simply for cooling purposes, and must not be too deep, or your dish will be liable to crack. Now add about 5 cc. of bromine water to your alcoholic solution, pouring it down the side of the dish carefully, so it will run under the alcoholic solution, without mixing any more than can be helped. Then simply light the alcoholic solution with a match. The alcohol will burn off in from 10—15 minutes. The water outside prevents the solution from getting too hot and spattering.

When the solution has burnt out and cooled, add 10 cc. concentrated solution of ammonium chloride. A few drops of rosolic acid solution as indicator are now added, and ammonia water till distinctly red.

The dish is transferred to the water-bath, and heated until the red colour is changed to a yellow. A little hot water is used to mix and dissolve any crusts that may have formed. Use water as hot as possible, and just before putting on the filter add ammonia very cautiously till it is faintly pink, and mix well by squirting in a fine stream from your wash-bottle. Then throw on a good tight 12½ cm. filter (either S and S 589 or Munktell's 00) and let it all run through before adding the rinsings from the evaporating dish. The washing should be done without disturbing the layer of precipitate on the filter, and the water used should be as nearly boiling as possible. Usually (unless the percentage is very high), about three to four washings are sufficient to remove all the foreign matter.

The moist precipitate on the filter is now placed in a 20 cc. platinum crucible, and dried over a very low flame. Then it is charred at a low red (don't let it catch fire) and finally ignited over a good Bunsen.

The weight of this precipitate is equivalent to the weight of the phosphate of iron plus phosphate of alumina. In most of the older contracts one-half of this weight was the figures referred to when speaking of oxides of iron and aluminium "combined."

It must be remembered, that in case only 75 cc. were operated on, that correction should be made to figure proper percentages from ¾ to 1 grm. This matter of taking one-half the weight of the phosphates to be the oxides of iron and alumina, "combined," has been sanctioned by custom, but is manifestly incorrect. It is therefore necessary to separate at least the iron in order to get at the actual percentages.

To do this the ignited oxides in the platinum crucible are dissolved in dilute sulphuric acid on the hot plate. The solution takes place easily, leaving only a skeleton of filter ash.

This solution can be made up to 100 cc., and the iron titrated in, say, 50 cc. with permanganate, and in the other 50 cc. the phosphoric acid, or the alumina, may be determined. Then it is a simple matter of calculation to get at the actual percentages of iron and alumina in the sample under examination.—*Journal of Industrial and Engineering Chemistry*, i., No. 7.

OCCURRENCE OF FORMALDEHYDE IN SUGAR-CANE JUICE AND SUGAR-HOUSE PRODUCTS.

By P. A. YODER and W. G. TAGGART.

In an investigation on some minor constituents of the sugar-cane and sugar-house products, we diverged from the main branch of the problem pursued (the acid constituents) to investigate the occurrence of formaldehyde, and incidentally for the further elaboration of a method for quantitatively estimating small amounts of formaldehyde. We were led to this side-line investigation by a consideration of the facts (1) that formaldehyde is very convenient to use, and frequently is used to preserve fresh juice in the sugar-house when boiling is interrupted from any cause; (2) that it is recommended by some as a clarifying agent; (3) that formaldehyde is objectionable in food products; and (4) that it has never, so far as we know, been proved, but is generally assumed that it all boils away in the evaporation of the juice to a massecuite. Further complicating the problem are some recent reports that in caramelising sugar, or even in boiling sugar solutions, formaldehyde is formed. Trillat (*Comptes Rendus*, cxlii., 454; *Chem. Centr.*, 1905, i., 18, 131, 1178, 1423; 1906, i., 917, 1193; *Zeit. Ver. Rübenzucker Ind.*, 1906, 93; *Bull. de. l'Assoc. des Chim. de Sucr. et de Dist.*, xxiii., 649) and A. A. Ramsey (*Journ. Roy. Soc. N.S.W.*, 1907, xli., 172; *Intern. Sugar Journ.*, xi., 100; *Bull. de l'Assoc. des Chim. de Sucr. et de Dist.*, xxvi., 587) report thus. Chas. H. La Wall (*Am. Journ. Pharm.*, lxxxi., 384; *Chem. Abstr.*, iii., 2836) calls into question the conclusions of Trillat and Ramsey, pronouncing the test which the latter used as unreliable. That formaldehyde can form unstable compounds with some of the sugars has been reported by several investigators. Lippmann (*Chem. d. Zuckerarten*, ii., 1320) mentions such a compound with cane-sugar.

The preliminary work on the detection of the formaldehyde in sugar-house products and on the quantitative methods for its estimation was done by us jointly, the junior author carrying out most of the laboratory tests. The working out of final details of the quantitative method used and its application to the juices and sugar-house products reported here was done by the senior author, who alone and in a private capacity is responsible for the formulation of this report and the conclusions drawn.

Methods for Detecting and Estimating Formaldehyde.—Of qualitative tests for formaldehyde there is no lack, and many of them are exceedingly delicate. The reliable quantitative methods usually mentioned in text-books, *e.g.*, the KCN and $AgNO_3$ method, or the H_2O_2 acidimetric method, are not sufficiently delicate to use with the very small quantities with which we found it desirable to work. Hehner's test with milk and concentrated H_2SO_4 containing a trace of iron, as well as a similar test with HCl, seems to be characteristic of formaldehyde, and so delicate for qualitative work that we were led to look hopefully to modifications of these for a quantitative method which, even if not extremely accurate, is sufficiently accurate and delicate for our purposes. F. W. Richardson (*Journ. Soc. Chem. Ind.*, xxvi., 3 and 4; *Chem. Abstr.*, i., 750) modified Hehner's method to make it colorimetrically quantitative, using in place of milk a clear solution containing albumose, which he prepared by incompletely digesting egg albumen with a solution of pepsin and HCl. Seeking a similar substitute for milk in the method with ferruginised concentrated HCl, we tried first a solution of dried peptone, such as is used in bacteriological laboratories. This worked so satisfactorily that we did not take further trouble to prepare partly digested albumen. Substituting this peptone solution for milk, we had a very delicate reagent, and the resulting coloured solutions were so clear as to be well adapted for comparisons in Nessler's tubes.

In the preliminary work, 1 cc. of the distillate or other solution to be tested was mixed with 5 cc. of a 1 per cent peptone solution and 5 cc. of concentrated HCl containing

1 part $FeCl_3$ in 5000 parts acid. This mixture was gradually heated in a small flask over a free flame to from 80° to 85°, held at that temperature two minutes, and then allowed to cool. Thus we tested the following compounds closely related to formaldehyde or frequently accompanying it:—Acetic aldehyde, benzaldehyde, sucrose, dextrose, levulose, xylose, ether, ethyl and methyl alcohols, acetic, lactic, oxalic, propionic, glycolic, citric, and benzoic acids, phenol, metol, pyrogallol, furfurol, potassium cyanide, and acroleïn. Of these the glycolic acid and the ether are the only ones that gave the same colour. The same sample of ether, after being thoroughly washed, ceased to give it. We conclude that the ether was contaminated with formaldehyde and probably the glycolic acid likewise. After the publication of the article by La Wall above referred to, in which he assigns furfurol as the cause of Ramsey's supposed test for formaldehyde in caramelised sugar products, additional tests with furfurol were made according to the details as finally worked out for this method and reported below. Though applied to solutions of furfurol ranging in strength from 1 in 1,000,000 to 1 in 100, we got no reaction except the faint tint which water alone gives with the reagents. Assuming the ferruginised concentrated H_2SO_4 reacts or fails to react in the same cases, we must conclude that La Wall was in error, and that his furfurol actually had formaldehyde in it, but not in sufficient quantity to show in the less sensitive test of Rimini, upon which La Wall depended to prove the presence or absence of formaldehyde. As ultimately applied to cane juice and sugar solutions, our method in detail is as follows: –

The sugar solution is acidified with H_3PO_4, then distilled from a bath of boiling saturated common salt solution with a current of steam superheated to a temperature such that there will be but little change in the volume in the distillation flask. To 5 cc. of the distillate in a test-tube, size 20 mm. by 180 mm., add 5 cc. of a 1 per cent peptone solution (recently dissolved and filtered), and 10 cc. concentrated HCl containing 1 part $FeCl_3$ to 5000. Mix these with a heavy glass stirring rod with rounded end, which may conveniently remain in the tube to weight it down and aid in mixing while heating in the water-bath. Prepare likewise any number of other samples and at the same time a set of standards for comparison, which may conveniently include strengths 1 : 50000, 1 : 100000, 1 : 200000, 1 : 500000, 1 : 1000000, 1 : 2000000, and a blank. The test-tubes suspended through holes of an appropriate size in a board, are suspended in a water-bath previously heated to such a temperature slightly above 82·5° C. that the cold tubes will bring it down to about 82·5. Keep it in the bath at this temperature for altogether five minutes, occasionally shaking by a rotatory motion of the board so that the glass rods in the tubes will rotate and help mix the contents, then set into a bath of cold water. After cooling, the colour intensities of each sample and its most nearly matching standard are matched in the ordinary way by varying the depths of the columns in Nessler's tubes. From these data the strength of the sample is determined. If the sample is stronger than 1 : 100000 it should be diluted tenfold or a hundredfold before mixing and heating, to bring it within the range 1 : 100000 and 1 : 1000000. As the dilute solutions of formaldehyde do not keep well, the tests should be made not too long after distilling and the standards should be made up from strong solutions not over a day or two prior to the time of using them.

An extended study of this method developed the following facts :—

Blanks with the reagents available to us always gave a slight coloration, barely distinguishable from that with a standard 1 : 5000000. Practically the method is not applicable to solutions weaker than 1 : 1000000.

With solutions of formaldehyde stronger than 1 : 100000 and reagents of same strength as before indicated, the increase in intensity of colour is not correspondingly great. Instead of a deeper colour, it develops a colour less towards the violet and more towards the purple shade. Diluting afterwards to like strengths will not bring such pairs to like intensities of colour.

Stronger solutions of formaldehyde with reagents stronger in both peptone and $FeCl_3$ will develop a correspondingly greater intensity of colour.

The proportion of $FeCl_3$ to the peptone should not vary greatly from that given above to get best results.

Nitric acid may be substituted as the oxidising agent for $FeCl_3$, using 1·6 cc. normal HNO_3 to 100 cc. concentrated HCl, as was done by Shrewsbury and Knapp (*Analyst*, xxxiv., 12; this report came to our attention after practically all our work on the method was completed), but, contrary to the conclusions of these gentlemen, we did not find the HNO_3 possessing any advantage, but having the disadvantage of decomposing and losing its activity quickly on standing after mixing with the HCl.

With the water-bath as low as Shrewsbury and Knapp report, viz., 50°, we found the action too feeble to be satisfactory, and likewise at 66°.

The colour, after cooling, changes very slowly towards blue and less intensity, allowing one or two hours after heating to make the comparisons, provided, however, that sample and standard stood equally long.

Heating the mixture over the free flame in a casserole, controlling the temperature by the aid of a thermometer, gave less good results, and was far less expeditious where many samples and standards had to be prepared.

In these experiments, in which superheated steam was used, the steam was superheated, for want of a better way, by passing it through a copper spiral over a small flame. Its temperature was controlled by use of a thermometer in the current of the steam about 5 inches above the neck of the distillation flask, and about 10 inches from the liquid through which it bubbled. The temperature at the thermometer was held at about 115°, never going above 120°, except in Nos. 5, 7, 9, and 10, in which it was held at 120° to 125°. With the distillation flask in a boiling water-bath and the inflowing steam at 115°, the volume increased about 9 cc. for every 50 cc. distilled. With the boiling saturated brine-bath and the steam at 115°, the volume decreased about 7 cc. for every 50 cc. distilled. Though we adhered in most of these tests, for the sake of uniformity and comparative results, to the one temperature, 115°, our recommendation is to choose a lower temperature, or, if necessary, to omit superheating the steam, so that the volume in the distillation flask may remain constant.

Application in Examination of Cane Juices, Sugar-house Products, and Special Mixtures.—The test for formaldehyde, of course, could not be made in the presence of the sugar and other constituents of the juice, therefore distillation was necessary to separate the formaldehyde from interfering substances. Experiments were tried with and without previously acidifying and by distillations from free flame, from oil-bath, by steam from oil-bath, by superheated steam from water-bath, and by superheated steam from brine-bath.

In the preliminary work, while we were following the method of heating over the free flame and comparing samples and standards that were prepared in succession, the results were not always regular or conclusive, but among the following conclusions, those not based upon the results of the final tests reported in the accompanying table are based upon regularities in the results of the preliminary tests, such as seemed to justify the conclusions.

In all the distillations the mouth of the condensers touched, or nearly touched, the narrow neck of the receiver flask, but no further provision was made to guard against the escape of formaldehyde into the air.

In tests in distilling in this manner, moderately strong formaldehyde solutions (1 per cent), acidified with phosphoric acid, and determining the formaldehyde in the distillate by the KCN—$AgNO_3$ method, the recoveries were 84, 91, and 102 per cent respectively in three tests.

If water is distilled with superheated steam from a 10 or

Table of Formaldehyde Determinations.

No. of test.	Composition of mixture.	Formaldehyde found in fractions of distillate. In first 50 cc. Mgrm.	In second 50 cc. Mgrm.	In third 50 cc. Mgrm.	In fourth 50 cc. Mgrm.	In fifth 50 cc. Mgrm.	CH_2O recovered. Mgrm.
	Manner of Distillation: Direct over flame.						
1.	200 cc. juice + 5 cc. H_3PO_4 (*a*)	0·025	0·100	0·250	—	—	0·375
1A.	Residue from 1 + 170 cc. water	0·50	0·50	0·50	—	—	1·50
2.	200 cc. juice + 2 mgrms. CH_2O + 5 cc. H_3PO_4 .	0·86	0·94	0·96	0·30 in 15 cc.	0·16 in 6 cc.	3·22
2A.	Residue from 2 + 170 cc. water	0·50	0·50	0·50	—	—	1·50
3.	200 cc. juice + 2 mgrms. CH_2O	0·39	0·81	0·66	0·19 in 15 cc.	0·08 in 6 cc.	2·13
3A.	Residue from 3 + 170 cc. water	0·62	0·63	0·57	—	—	1·82
4.	20 grms. Sugar I. (*b*) + 200 cc. water + 5 cc. H_3PO_4..	0·059	0·190	0·270	—	—	0·519
	Superheated steam and in water-bath.						
5.	10 grms. Sugar I. + 100 cc. water..	0·009	0·010	0·009	—	—	0·028
6.	Duplicate of 5	0·012	0·011	0·011	—	—	0·034
7.	10 grms. Sugar I. + 100 cc. water + 5 cc. H_3PO_4	0·025	0·028	0·027	0·027	—	0·107
8.	Duplicate of 7	0·021	0·027	0·028	—	—	0·076
9.	10 grms. Sugar I. + 100 cc. water + 1 mgrm. CH_2O	0·36	0·35	0·20	0·21	—	1·12
10.	10 grms. Sugar I. + 100 cc. water + 1 mgrm. CH_2O + 5 cc. H_3PO_4	0·53	0·37	0·21	0·18	—	1·29
	Superheated steam and in brine bath.						
11.	15 grms. Sugar II. (*c*) + 100 cc. water..	0 008	0·008	0·008	—	—	0·024
12.	15 grms. Sugar II. + 100 cc. water + 5 cc. H_3PO_4	0·025	0·025	0·028	0·033	0·032	0·143
13.	15 grms. Sugar II. + 100 cc. water + 1 mgrm. CH_2O + 5 cc. H_3PO_4	0·46	0·27	0·14	0·09	0·08	1·04
14.	15 grms. sugar run, after 5, made without CH_2O + 100 cc. water + 5 cc. H_3PO_4	0·000 (*d*)	0·025 (*d*)	0·028	0·043	0·047	1·43
15.	15 grms. sugar, run 6, made with CH_2O + 100 cc. water + 5 cc. H_3PO_4	0·007 (*d*)	0·030 (*d*)	0·047	0·054	0·054	0·192
16.	15 grms. molasses run 5, made with CH_2O + 100 cc. water, + 5 cc. H_3PO_4	0·000 (*d*)	0·008 (*d*)	0·031	0·028	0·025	0·092
17.	15 grms. molasses, run 6, made with CH_2O + 100 cc. water + 5 cc. H_3PO_4..	0·027 (*d*)	0·100 (*d*)	0·118	0·123	0·100	0·468

(*a*) The H_3PO_4 solution in each case was an 85 per cent solution.
(*b*) Sugar I. is commercial refined sugar from the local market.
(*c*) Sugar II. is commercial sugar from India.
(*d*) In these fractions of the distillate there was a slight cloudiness, and probably interference with the test.

15 per cent sugar solution, not acidified, there are only traces of formaldehyde shown in the distillate (Nos. 5, 6, and 11 in the table).

In distilling an acidified juice or sugar solution from the direct flame (Nos. 1 and 4), the succeeding fractions of the distillate increase in the amount of formaldehyde as the caramelisation point is approached. The browned residue, re-dissolved and again subjected to distillation, yields distillates relatively strongly charged with formaldehyde (Nos. 1A, 2A, 3A). These results seem to bear out the conclusions reached by Trillat and Ramsey, cited above, with reference to the formation of formaldehyde in the caramelisation of sugar. However, we are still not quite sure that this caramelisation product, the distillate from which gives the formaldehyde reaction, is actually formaldehyde, though we are satisfied it is not furfurol. It does seem strange, if formaldehyde is formed by very slight caramelisation in such large quantities as indicated by Nos. 1A and 2A in the table, that jams, caramel candies, and many other sweetmeats can be eaten with such impunity as they are.

In distilling sugar solutions with superheated steam, the distillates show only traces of formaldehyde, and succeeding fractions are nearly constant in formaldehyde content (Nos. 7 and 12). In 250 cc. of distillate with superheated steam through a solution of 15 grms. sugar in 100 cc. water, only 0·143 mgrm. formaldehyde was formed.

A number of other samples of fresh juice not recorded in the table, including one from green top joints of cane, gave results not remarkably different from No. 1 here reported.

In preliminary tests in which formaldehyde was added to water and to sugar solutions, there was evidence that sugar tended to hold back a small portion of the formaldehyde from distilling over.

Adding formaldehyde to cane-juice or sugar solutions in the proportion of 1 mgrm. per 100 cc., it is recovered in the distillate either from direct distillation or from distillation with steam, in such amounts that the tests, quantitatively applied, can serve easily to distinguish between products to which it has, and those to which it has not been added (Nos. 2, 10, and 13, and Nos. 1, 4, 7, and 12). From these acidified formaldehyde solutions, the formaldehyde comes off most copiously in the first fractions. When not acidified this is less marked, and the total recovery is less in the same total volume of distillate (*cf.* Nos. 3 and 9). When made alkaline with NaOH, as we did in some preliminary trials, the tendency to hold back formaldehyde in the sugar solution was many fold greater.

Coming now to the main question which concerned us, viz., Does formaldehyde added to juice in the sugar-house

all boil away or does it persist in any final saleable products? we seek the answer in tests Nos. 14 to 17.

Runs 5 and 6 were made at the small mill of the Louisiana Sugar Experiment Station, the former without the addition of any formaldehyde either in that or the immediately preceding run, and the latter with the addition of formaldehyde to the fresh juice in the proportion of about 1 part of formalin (40 per cent sol. of formaldehyde) to 160,000 parts of juice, or 25 parts CH_2O to a million. The clarification in each run was as usual with sulphurous acid, followed by liming back almost to neutrality. The concentration was accomplished as usual with reduced pressure in the "effects" and vacuum pan. The sugars used in these experiments (Nos. 14 and 15) are the first sugars, testing about 96 per cent, and the molasses samples (Nos. 16 and 17) are of the first molasses in each case, testing about 43 per cent sucrose and 58 purity. In the distillation with superheated steam and the formaldehyde determination in these samples, carried out as above described, a peculiar condition developed which was not noted in the previous samples with pure sugar solutions. The first one or two fractions of the distillate, were slightly cloudy, and these same fractions, which should have been highest in formaldehyde, gave no reaction, or only very weak ones for that substance. This leads us to suspect that our test in these cases does dot show the total quantities of formaldehyde present. Suspecting that the interfering substance may be sulphurous acid, or possibly other sulphur compounds, tests were made, and it was found that the addition of sodium sulphite strongly interfered, that sodium thiosulphate completely prevented the colour development, and that hydrogen sulphide but slightly affected the intensity of the reaction. Notwithstanding these probable shortages in the total formaldehyde recovered, we still find evidence of an excess of formaldehyde in the products from juice to which it had been added, very small in the case of the first sugar, but more pronounced in the case of the first molasses. In the first sugar it amounts to 12·8 parts CH_2O per million as against 9·5 parts per million in first sugar from juice without added formaldehyde, or an excess of 3·3 parts per million. In the first molasses it amounts to 31·2 parts per million as against 6·1 parts per million in first molasses from juice without added formaldehyde, or an excess of 25·1 parts per million. The molasses is thus found to be as strongly charged with this excess of formaldehyde as was the juice from which it was made. Assuming that the yields of first sugar and first molasses are 9·5 per cent and 6 per cent respectively of the juice, then the amounts of formaldehyde retained by them are about 1·2 per cent and 6 per cent respectively of that added to the juice, or a total of 7·2 per cent, which, as far as these tests show, was not boiled away. It is probable, as pointed out above, that these tests show only part of that actually retained. The small quantity left in this 96 per cent sugar may justify the conclusion that in refining the sugar this excess is all eliminated.

If the sugar is the only product used for food, then there need be no hesitation, on the score of health considerations, in using formaldehyde as a preservative in juice in the sugar-mill. If, however, the molasses is also to be used for food, or if table syrup is to be manufactured, then the question of the permissibility of its use may reasonably be raised. To this question we deem the data now at hand to be insufficient basis for a definite answer. We should have the results from further tests of final and of intermediate products. We should develop a method to circumvent the interference of sulphurous acid or other substances in the distillates, in the formaldehyde determination. We should make comparative tests also with syrup or molasses and sugar made by the open kettle method of boiling, with and without formaldehyde. We should, moreover, know in what form or combination the formaldehyde is held back in these sugar solutions, and whether it is deleterious to health in this form or combination.—*Journal of Industrial and Engineering Chemistry*, ii., No 6.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 30th, 1910.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*New Method for the Quantitative Estimation of Hydrocyanic Acid in Vegetable and Animal Tissues.*" By Prof. A. D. Waller, F.R.S.

The method is colorimetric, and depends on the reaction between potassium cyanide and picric acid, first studied by Hlasiwetz (*Liebig's Annalen*, 1859, cx., p. 289), and recently applied by Guignard to the detection of minute quantities of hydrocyanic acid (*Annales Sci. Pharmacol.*, 1906, p. 415), and by H. E. Armstrong to the rapid detection of emulsin (*Proceedings*, March 10).

The colour-scale is prepared by mixing equal volumes of a recently titrated solution of 1/10000 hydrocyanic acid and of picrate mixture (equal volumes of 0·5/100 picric acid and 5/100 sodium carbonate). From this stock solution (T 50), after twenty-four hours in an incubator at 40°, a colour-scale is prepared by further dilution with picrate mixture, to contain, *e.g.*, 1, 2, 3, &c., parts of HCN per million, of tints T 1, T 2, T 3, &c.

The estimation is made by matching the colour of the given fluid or of its distillate into picrate mixture (after suitable dilution if required), with that of the colour-scale.

Thus, *e.g.*, if the tint of a distillate from 10 cc. of blood (dil. × 5) into 25 cc. of picrate is found = T 5, and the volume of picrate + distillate is 40 cc., the amount of HCN in the distillate = 5 × 40 millionths grm., *i.e.*, 0·000200. A second distillation shows whether or no the whole of the HCN present has been taken over in the first distillate.

Results of the application of the method to—(1) A leaf of *Prunus Laurocerasus*; (2) the blood and tissues of a cat after death by a known amount of HCN; (3) the blood and tissues of a person "found dead."

"*Structure, Development, and Morphological Interpretation of the Pineal Organs and Adjacent Parts of the Brain in the Tuatara* (Sphenodon punctatus). By Prof. A. Dendy, F R.S.

"*Scattering of Homogeneous β-rays, and the Number of Electrons in the Atom.*" By J. A. Crowther, M.A., Fellow of St. John's College, Cambridge.

1. The scattering of a homogeneous pencil of β-rays has been measured for various substances and for rays of different velocity. It has been shown to obey the following statistical laws:—

   i. For rays of given velocity the intensity I of the radiation contained within a given cone may be expressed by the equation $I/I_0 = 1 - e^{-kt}$, where t is the thickness of material passed through, and k a constant depending upon the angle of the cone.
   ii. For rays of given velocity the most probable angle of emergence is proportional to the square root of the thickness of material traversed by the rays.
   iii. For rays of different velocities the probable angle of emergence divided by the square root of the thickness traversed is inversely proportional to the product of the mass of the incident β-particle into the square of its velocity.

2. From equations given by Prof. Sir J. J. Thomson the number of electrons contained in atoms of different elements is deduced. It is thus found:—

   i. That the ratio of the number of electrons per atom to the atomic weight is constant; the ratio being very nearly 3·0 for all the elements examined.
   ii. That the positive electricity within the atom is not in an electronic condition, but is distributed fairly uniformly over the space occupied by the atom.

3. Experiments are described on the absorption of homogeneous β-rays. It is shown that the first stage in the absorption of a *pencil* of homogeneous β-rays consists in the scattering of the rays according to the laws already considered. The absorption of the completely scattered radiation is then shown to take place according to an exponential law.

"*Spontaneous Crystallisation and the Melting and Freezing-point Curves of Mixtures of Two Substances which form Mixed Crystals and Possess a Minimum or Eutectic Freezing-point. – Mixtures of Azobenzene and Benzylaniline.*" By Miss F. ISAAC.

The results obtained in this research may be thus summarised :—

1. The freezing and melting-point curves for mixtures of azobenzene and benzylaniline have been determined, and it has been shown that these substances possess a minimum or eutectic point at 26° for the mixture containing 19 per cent azobenzene and 81 per cent benzylaniline, and form a series of mixed crystals on one side only of the eutectic, viz., that with excess of azobenzene. This is, therefore, a limiting case of Roozeboom's Type 5, in which two substances, A and B, possess freezing and melting-point curves which exhibit a minimum eutectic point, and form two series of mixed crystals, *i.e.*, mixed crystals containing excess of A, and mixed crystals containing excess of B.

2. The melting-point curve has been confirmed by actual analysis of the mixed crystals.

3. The supersolubility curve, or curve of spontaneous crystallisation, has been determined for these mixtures by two methods :—(1) By noting the temperature at which a liquid mixture of known composition crystallises spontaneously in a sealed tube; (2) by noting the temperature at which a known liquid mixture attains its highest refractive index and gives a dense labile shower when placed in the trough of the inverted goniometer. It has been shown that each mixture possesses a definite temperature of spontaneous crystallisation.

The supersolubility curve shows a minimum for liquids having approximately the eutectic composition, and runs approximately parallel to the freezing-point curve. It crosses the melting-point curve three times.

The nature of the mixed crystals which first separate spontaneously from any liquid mixture on the supersolubility curve has been investigated. The composition of such crystals has been determined by separating them from their mother-liquor and finding their melting-points.

5. A few thin sections have been ground from the solid mixtures in the neighbourhood of the eutectic, and their structures examined. These structures do not appear to be permanent. After the lapse of some months they completely changed, new crystal needles appearing all over the sections. These changes, however, appear to be very gradual, and to take place with change of temperature.

"*Determination of the Chief Correlations between Collaterals in the Case of a Simple Mendelian Population Mating at random.*" By E. C. SNOW.

This paper investigates the values which should hold for the correlations between (*a*) siblings, (*b*) uncle and nephew, and (*c*) first cousins, on the Mendelian hypothesis of "unit-characters."

The correlations both for gametic and somatic characters are found. For the former, values independent of the distribution of the dominant and recedant characters among the population are obtained. These are (*a*) 0·500, (*b*) 0·250, and (*c*) 0·250. In the case of the somatic correlations, however, the results depend upon the relative numbers of the population possessing the dominant and recedant attributes before crossing. By varying this proportion different values of the correlations can be obtained, but these are always less than the corresponding gametic ones stated above.

The investigation brings out the important point that on the Mendelian theory of heredity the similarity between first cousins is quite as close as, or closer than, those between uncle and nephew. Biometric results previously reached have pointed to the same conclusions. This is of great interest from the medical point of view. In medical diagnosis a man's uncles and aunts, but not his cousins, are generally considered. But the results of the present paper show that his cousins, usually more numerous, give just as good a knowledge of his constitutional tendencies as do his uncles and aunts.

"*Propagation of Sound in a Fog.*" By C. J. T. SEWELL, M.A., Trinity College, Cambridge.

This paper is intended as a sequel to my previous paper on "The Extinction of Sound in a Viscous Atmosphere by Small Obstacles of Cylindrical and Spherical Form," in which the loss of energy from the primary waves owing to viscosity was investigated. In the present paper I have included the additional loss of energy due to heat conduction. The work proceeds on much the same lines as before, and the results obtained are of the same order of magnitude. The chief interest consists in the application of the results to the effect of atmospheric fog upon the propagation and audibility of sound. Waves of high frequency suffer most. If the diameter of the drops of water in a dense fog is assumed to be 0·02 mm., and the density of the fog amounts to 4½ grms. per cubic metre, the intensity of sound of wave-length 100 cm. is reduced in the ratio of 1 to *e* before the sound has travelled a distance of 100 metres. If the wave-length is 1000 cm., this distance is increased to about 350 metres. In any case the results seem to show that the presence of fog at sea must diminish quite appreciably the audibility of sound.

"*Determination of the Ratio of Mass to Weight for a Radio-active Substance.*" By L. SOUTHERNS.

A determination has been made of the ratio of mass to weight for uranium oxide by comparison with the known value for a normal substance (lead oxide). It had been supposed by Sir J. J. Thomson that a radio-active substance might possess greater mass than the same weight of a non-radio-active substance, on account of the greater store of potential energy which is associated with the former. In the case of uranium oxide the increase in the ratio of mass to weight would be about 1 in 16,000.

The investigation has been made by means of a rigid pendulum fitted with two knife-edges and a hollow bob into which could be packed either of the substances used. Special means have been employed in order to eliminate errors due to slight variations in the position of the centre of gravity of the pendulum, and to other causes. The results show that the ratio for the uranium oxide does not differ from the normal value by more than 1 in 200,000, and thus that the contemplated effect is absent.

"*Relative Atomic Weights of Nitrogen and Sulphur.*" By F. P. BURT and F. L. USHER.

The object of the research was to determine the combining weights of nitrogen and sulphur by the analysis of nitrogen sulphide. The method adopted was briefly as follows :—A weighed quantity of nitrogen sulphide, purified by sublimation *in vacuo* over silver at 100° C., was decomposed by subliming over red-hot quartz wool contained in a quartz tube. The sulphur was deposited a few inches beyond the wool and the nitrogen was pumped off and estimated in a constant-volume gas burette. Assuming the density of nitrogen, the relative weights of nitrogen and sulphur could be calculated, the sulphur being obtained by difference.

The problem was complicated by the impossibility of starting an experiment with the quartz wool in the reaction tube in a gas-free condition. The difficulty was overcome by measuring in blank experiments the quantity of air removable from the hot wool *in vacuo*, and by estimating traces of more condensable gas present by exposing the nitrogen to potash and re-measuring it. The final corrected N/S ratios are as follows, the weight of a "normal litre" of nitrogen in London being taken as 1·25144 grm. : —0·436847, 0·436875, 0·436839, 0·436857, 0·436897, 0·436878, 0·436898.

The mean is 0·436870, and the greatest deviation from the mean is 1 in 14,000. From this ratio the atomic weight of sulphur becomes 2·067, if nitrogen be given the very probable value 14·009.

"*Relation of Light Perception to Colour Perception.*" By F. W. Edridge-Green, M.D., F.R.C.S., Beit Medical Research Fellow.

It may be easily shown that light perception and colour perception are quite distinct. In fact, we can divide cases of colour-blindness into two classes according as the defect is (*a*) one of light perception, or (*b*) one of colour perception or differentiation without any defect in light perception. Of course, both defects may be present in the same individual.

The investigation of these two classes of defective vision is much facilitated by the use of a spectrometer which I have devised for the purpose. This instrument is a spectrometer so arranged as to make it possible to expose to view in the eye-piece the portion of a spectrum between any two desired wave-lengths. Tested with this instrument a normal individual will, as a rule, name six distinct colours, namely, red, orange, yellow, green, blue, and violet, and will mark out by means of the shutters about eighteen monochromatic patches.

Occasionally we come across individuals with a greater power of differentiating hues, to whom, as to Newton, there is a distinct colour between the blue and violet, which Newton called indigo. Such individuals will mark out a greater number of monochromatic patches, from twenty-two up to twenty-nine.

Those who have defective light perception for certain rays, with normal hue perception, behave exactly in the same way as a normal-sighted person with those rays removed or reduced to the same intensity, and not as if a light-perceiving substance which was sensitive to rays from a considerable range of the spectrum had been removed.

Those with defective hue perception mark out with the spectrometer a smaller number of monochromatic patches than the normal, and say that there are five, four, three, two, or one colour instead of the normal six. They behave in every way as if their colour sensations were correspondingly limited. Therefore, if the normal be designated hexachromic, then pentachromic, tetrachromic, trichromic, dichromic, or monochromic correctly describes their colour-vision.

"*Anatomy and Morphology of the Leaves and Inflorescences of* Welwitschia mirabilis." By M. G. Sykes, Girton College, Fellow of Newnham College, Cambridge.

"*The Natural Food of* Glossina palpalis." By Colonel Sir David Bruce, C.B., F.R.S., Army Medical Service; Captains A. E. Hamerton, D.S.O., and H. R. Bateman, Royal Army Medical Corps; and Captain F. P. Mackie, Indian Medical Service (Sleeping Sickness Commission of the Royal Society, Uganda, 1908-10).

"*Mechanical Transmission of Sleeping Sickness by the Tsetse Fly.*" By Colonel Sir David Bruce, C.B., F.R.S., Army Medical Service; Captains A. E. Hamerton, D.S.O., and H. R. Bateman, Royal Army Medical Corps; and Captain F. P. Mackie, Indian Medical Service (Sleeping Sickness Commission of the Royal Society, Uganda, 1908-10).

"*Comparative Toxicity of Theobromine and Caffeine as Measured by their Direct Effects upon the Contractility of Isolated Muscle.*" By V. H. Veley, F.R.S., and A. D. Waller, F.R.S.

It is shown by measurements of the contractility of isolated muscle that the toxicity of theobromine, the base of cocoa, is greater than that of caffeine, the base of coffee and tea, in the proportion of 3 : 2.

The introduction of a second methyl group into the oxypurine residue, namely, the formation of caffeine from theobromine, thus diminishes the toxic value, a result which is the converse of that observed in the case of the paraffinoid alcohols.

The toxic effects of coffee and tea extracts are also studied, and it is shown that the effect of the former is mainly due to the caffeine contents and not to the tannic acid.

"*Assimilation of Nitrogen by certain Nitrogen-fixing Bacteria in the Soil.*" By W. B. Bottomley, M.A., Professor of Botany in King's College, London.

"*Inorganic Composition of the Blood in Vertebrates and Invertebrates and its Origin.*" By Prof. A. B. Macallum, F.R.S.

"*Origin and Destiny of Cholesterol in the Animal Organism.* Part VII. *On the Quantity of Cholesterol and Cholesterol Esters in the Blood of Rabbits fed on Diets containing Varying Amounts of Cholesterol.*" By Mary T. Fraser, B.Sc., and J. A. Gardner, M.A.

CHEMICAL SOCIETY.

Ordinary Meeting, June 16th, 1910.

Prof. Harold B. Dixon, M.A., Ph.D., F.R.S., President, in the Chair.

Messrs. A. Clayton, Frederick C. Lewis, and Charles Proud were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Henry Vincent Aird Briscoe, B.Sc., 33, Bargery Road, Catford, S.E.; David Jackson MacGeorge, Rangoon Refinery Co., Ltd., Thilawa, Burma; Alec Duncan Mitchell, B.Sc., Carnock, Hartley Road, Leytonstone, N.E.; William James Pittock Smith, 9, Meddowcroft Road, Gerard Road, Wallasey; Claude Vareille Temperley, B.Sc., Trent College; Richard Babington Turbutt, B.A., Royal Artillery Mess, Woolwich; Herbert Goulding Williams, B.Sc., Robert Gordon's College, Aberdeen; William Norman Stewart Wright, 26, Lansdowne Crescent, Glasgow, W.

A certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Prof. Leo Tschugaeff, The University, St. Petersburg.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Ward Allen Batley, M.Sc.; Geoffrey Alfred Bracewell; Ronald Leslie Collett, B.A.; Middleton Henry Dand; Alexander Scott Dodd, B.Sc.; James Grieve; Charles Frederick Guhlmann; John Edward Hackford, B.Sc.; John Haycock; John Huck, M.A.; Lionel Leslie Jacobs; Govind Laxmann Joshi; Frank Stevenson Long, B.Sc.; William Ernest Martin; Benjamin Mason Narbeth, B.Sc.; Robert O'Field Oakley; Edward Talbot Paris; John Alexander Reddie; Walter William Reed, M.Sc.; John George Rose; St. Clair Overbeck Sinclair, M.A.; Roland Edgar Slade, M.Sc.; James Harry Smith; Thomas May Smith; Kaikhushroo Bamanji Sorabji; Ernest Stedman, B.Sc.; Ferdinand Bernard Thole, B.Sc.; Frederick George Williams; John Williams, B.Sc.

Of the following papers, those marked * were read:—

*170. "*Studies of Dynamic Isomerism.* Part XII. *The Equations for Two Consecutive Unimolecular Changes.*" By Thomas Martin Lowry and William Thomas John.

The problem considered is that of a reversible isomeric change of the type $A \rightleftarrows B \rightleftarrows C$, in which the intermediate compound, B, is formed in quantities comparable with those of the initial material, A, and the final product, C. Equations are deduced for the changes of concentration with time in the case of each of the three substances: (*a*) when the sum of the concentrations is constant, as in an ordinary "mutarotation" experiment, and (*b*) when the concentration of the initial material is kept constant; for example, by saturation with the solid. The curve con-

necting concentration with time in the case of the compound C is inflected in character, the position of the point of inflexion depending on the four velocity constants corresponding with the four arrows of the above equation. Curves, showing the point of inflexion and the tangent at this point, have been drawn for a number of typical cases.

*171. "*Studies of Dynamic Isomerism.* Part XIII. *Camphorcarboxyamide and Camphorcarboxypiperidide.*" By Walter Hamis Glover and Thomas Martin Lowry.

Camphorcarboxyamide, $C_8H_{14}<^{CH\cdot CO\cdot NH_2}_{CO}$, prepared by heating the methyl ester with aqueous ammonia in a sealed tube at 100°, crystallises well from benzene, heptane, or light petroleum, melts at 118°, and gives an indigo coloration with ferric chloride. Changes of rotatory power are observed in freshly-prepared solutions of the amide in heptane, benzene, and alcohol. The solubility in heptane at 20° shows an analogous change, from 0·38 to 0·80 per cent, in the course of the first hour or two after the solvent is added, indicating that the initial material forms about 48 per cent of the final product.

The *bromoamide*, $C_8H_{14}<^{CBr\cdot CO\cdot NH_2}_{CO}$, melts at 114°, and gives no coloration with ferric chloride.

The *piperidide*, $C_8H_{14}<^{CH\cdot CO\cdot NC_5H_{10}}_{CO}$, prepared by the action of piperidine on the ester, melts at 106°, and gives a greenish coloration with ferric chloride. Changes of rotatory power are observed in freshly prepared solutions in heptane, benzene, and alcohol, but the mutarotation curves do not obey the unimolecular law, and the curves for solutions in benzene are strongly inflected; the abnormal character of the curves is attributed to the occurrence of two consecutive isomeric changes. The solubility in heptane increases from 2·06 to 4·66 per cent, and the proportion of the initial material in the final product is taken to be about 44 per cent.

The *bromo-piperidide*, $C_8H_{14}<^{CBr\cdot CO\cdot NC_5H_{10}}_{CO}$, melts at 132°, gives no coloration with ferric chloride, and undergoes no changes of rotatory power in freshly-prepared solutions.

Discussion.

Mr. Baly asked what evidence Dr. Lowry had that the compounds described exist in the enolic form. It appeared to him that the results described by Dr. Lowry in his last two papers (*Trans.*, 1910, xcvii., 899 and 905) were capable of another explanation, and that the existence of the enolic form was not proved by the spectroscopic observations. Of course these remarks did not influence in any way the value of the curves under discussion, but Mr. Baly questioned the advisability of assuming the existence of the enolic modifications if this assumption were only based upon the spectroscopic observations described in the previous work.

Dr. Senter asked, in reference to the observations on initial retardation, with what vessels the optically active substances had been in contact during the experiments.

In reply to Mr. Baly, Dr. Lowry said that in order to account for the inflected mutarotation curves it was only necessary to assume two successive isomeric changes in compounds of approximately equal stability. The intermediate compound was probably enolic, but this was not essential. In reply to Dr. Senter, both glass and silica tubes had been used; the velocities of isomeric change varied considerably, but the general form of the curves was the same for high and for low velocities.

*172. "*A Simple Method of preparing Tetranitromethane.*" By Frederick Daniel Chattaway.

Tetranitromethane in nearly theoretical amount can be obtained, if a suitable procedure be adopted, by the interaction of nitric acid and acetic anhydride.

The action of nitric acid on acetic anhydride has been described as dangerously violent. This, however, is not the case unless the temperature at which they are brought together is unnecessarily high.

When nitric acid attacks acetic anhydride a mononitro-derivative is probably first produced which is so much more readily nitrated than the parent compound that action proceeds until the three hydrogen atoms of a methyl group have been replaced. The trinitroacetic acid formed by hydrolysis then slowly decomposes into carbon dioxide and nitroform, which is converted as soon as it is liberated into tetranitromethane.

The methods adopted in preparing, isolating, and purifying tetranitromethane were described.

The necessary operations are so simple and so easily carried out that the preparation is well adapted to take its place in any elementary course of practical organic chemistry to illustrate the ease with which aliphatic compounds can be nitrated, whilst the materials employed are so cheap and the yield is so satisfactory as to make tetranitromethane, which has hitherto been a somewhat unfamiliar substance, one of the most easily procurable of organic compounds.

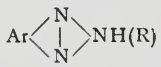
Discussion.

The President asked whether Dr. Chattaway had any proof of the formation of nitroform.

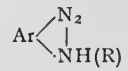
Dr. Chattaway said that he had no proof that nitroform was actually liberated as an intermediate product, but its formation appeared to be a necessary step in the series of reactions which must be assumed to take place. The conditions of interaction were such that it would be difficult, if not impossible, to recognise it as an intermediate product, since, in small amount, it was formed by the action of water on tetranitromethane.

*173. "*The Constitution of Ortho-diazoimines.* Part I. *The Naphthylenediazoimines and their Benzenesulphonyl Derivatives.*" By Gilbert T. Morgan and William Godden.

The authors' experiments had for their object the determination of the constitution of the ortho-diazoimines produced by the action of nitrous acid on the ortho-diamines. If the ortho-diazoimines and their acyl derivatives are to be represented by the general formula (I.),

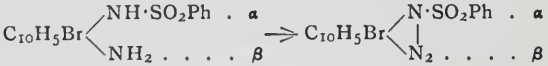


I.

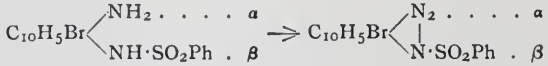


II.

then 1-*benzenesulphonyl*-4-*bromo*-1 : 2-*naphthylenediamine* (III.) (m. p. 220°) and its isomeride, 2-*benzenesulphonyl*-4-*bromo*-1 : 2-*naphthylenediamine* (V.) (m. p. 171°), should yield the same diazoimide; but on treatment with nitrous acid they give rise respectively to the isomeric compounds, 1-*benzenesulphonyl*-4-*bromonaphthylene*-2-*diazo*-1-*imide* (IV.) (m. p. 159°), and 2-*benzenesulphonyl*-4-*bromonaphthylene*-1-*diazo*-2-*imide* (VI.) (m. p. 209°).



III. IV.



V. VI.

These results indicate that the ortho-diazoimines and their acyl derivatives are more correctly represented by the general formula (II.).

Further confirmation was obtained by a study of the diazoimino-derivatives of 1 : 2- and 2 : 3-naphthylenediamines.

*174. "*The Colour and Constitution of Diazonium Salts.* Part II. *Diazo-derivatives of* as-*Benzoylethyl*-1 : 4-*naphthylenediamine.*" By Gilbert T. Morgan and Edward G. Couzens.

as-*Benzoylethyl*-1 : 4-*naphthylenediamine*,—

$$NH_2 \cdot C_{10}H_6 \cdot N(C_2H_5) \cdot CO \cdot C_6H_5,$$

contains an ethyl group in the place of the more labile hydrogen atom of benzoyl-1 : 4-naphthylenediamine, $NH_2 \cdot C_{10}H_6 \cdot NH \cdot CO \cdot C_6H_5$, yet both these bases give rise to yellow diazonium salts of considerable stability.

It follows that the colour of these diazo-derivatives is not due to any departure from the normal diazonium type consequent on a migration of hydrogen.

In the benzene series, the corresponding diazonium salts of benzoyl-*p*-phenylenediamine and the *as*-benzoylalkyl-*p*-phenylenediamines, although exceptionally stable, are colourless (*Trans.*, 1909, xcv., 1319).

The appearance of colour among aromatic diazonium salts is due, not to changes in the diazo-residue, but to an increase in the complexity of the aromatic nucleus with which this group is associated.

Discussion.

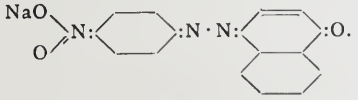
Dr. Hewitt stated that in view of the work just described, he fully accepted Dr. Morgan's conclusion that the *p*-acylaminodiazonium salts did not differ constitutionally from other diazonium salts.

*175. "*The Action of Alkalis on certain Derivatives of Coumarin.*" By Arthur Clayton.

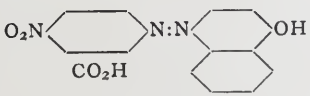
The action of alkalis on a number of nitro-derivatives of coumarin and its homologues has been investigated. Coumarins with a nitro-group in position 3 are converted by alkalis into the corresponding salicylaldehydes. If a methyl group is also present in position 4, a ω-nitro-α-methylstyrene is formed. Two new coumarinic acids have been isolated.

*176. "*The Relation between Absorption Spectra and Chemical Constitution.* Part XV. *The Nitrated Azo-compounds.*" By Edward Charles Cyril Baly, William Bradshaw Tuck, and Effie Gwendoline Marsden.

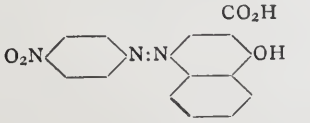
Hewitt and Mitchell (*Trans.*, 1907, xci., 1251) dealt with the ortho- and para-nitrobenzeneazophenols and nitrobenzeneazo-α-naphthols, and from the change in colour produced on the addition of alkali hydroxides concluded that the sodium and potassium salts have the di-quinonoid structure, as, for example:—



They also brought forward evidence to support this, based upon the two isomeric carboxy-derivatives I. and II., for the compound I. gives a blue lake with lead acetate, whilst II. gives a red one.



I.



II.

It has now been shown from a comparison of the nitrobenzeneazophenols and their sodium salts with the corresponding nitrobenzeneazodimethylanilines, benzeneazophenol, and its sodium salt, and with *p*-benzoquinoneazine, that the quinonoid explanation is incorrect. It is found that the carboxylic acids I. and II., as well as two other isomeric compounds which cannot possess two adjacent hydroxyl groups, give colloidal sodium salts. The solutions of these salts are precipitated by any metallic salt, as, for example, sodium chloride; the colour of these precipitates varies with the concentration, so that no conclusion whatever can be drawn as to two adjacent hydroxyl groups from the formation of insoluble precipitates with lead acetate.

Discussion.

Dr. Hewitt dissented from Mr. Baly's view as to the constitution of the salts of *p*-nitrobenzeneazo-α-naphthol and allied compounds. Benzeneazo-α-naphthol gave an alcoholic solution which, if sufficiently dilute, was yellow, and the colour was altered to a comparatively slight extent by the addition of alkali. Substitution derivatives of the type, $p\text{-}X \cdot C_6H_4 \cdot N{:}N \cdot C_{10}H_6 \cdot OH$ behaved in a similar manner, where X = Cl, CO_2Na, SO_3Na, &c., but where $X = NO_2$, $CH_3 \cdot CO\cdot$, or $H \cdot CO\cdot$, then addition of alkali produced a far larger displacement of the band of least frequency, with the result that purple or blue solutions were obtained. The first class of substituents did not allow of a quinonoid structure for the alkali salts, but this was possible with substituents of the second class. Another remarkable example was afforded by *p*-nitrobenzeneazosalicylaldehyde, the yellow alcoholic solution of which was but slightly affected on rendering alkaline; this was probably owing to salt formation taking place with quinonoid re-arrangement involving the aldehydo-group, so inhibiting the azobenzenequinone structure. Additional support was lent to this view by the fact that if the aldehydo-group was put out of action by conversion into a phenylhydrazone, addition of alkali produced an intense purple coloration.

Chemical properties were, however, far more important than optical in deciding questions of structure, and the observation made many years ago by Meldola, that *p*-nitro-substituted azophenols could be reduced smoothly to the corresponding amino-compounds by hydrogen sulphide in ammoniacal solution, showed that the ammonium salts of these *p*-nitro-compounds possessed a different structure from the unsubstituted parent substances with the true azo-linking, since the latter underwent fission at the double linking between the nitrogen atoms.

In reply to Dr. Hewitt, Mr. Baly drew attention to an interesting fact about the blue alkaline solution of *p*-nitrobenzeneazo-α-naphthol. In thin layers the solution was blue by transmitted light, but in thick layers it was pure red. This observation showed the danger of arguing entirely from visual colour. It appeared to him that Dr. Forster had drawn attention to the most important point, for the shifts observed on the addition of alkali to *o*-, *m*-, and *p*-nitrobenzeneazo-phenols and -α-naphthols were all very similar; indeed, *m*-nitrobenzeneazo-α-naphthol gave a greater shift than the *o*- and *p*-isomerides. Moreover, the shift given by benzeneazophenol was the same as that of the nitro-derivatives.

*177. "*Indirubin.*" (Part I.). By William Popplewell Bloxam and Arthur George Perkin.

In order to study the conditions necessary for the formation of indirubin by the air-oxidation of indoxyl, the authors have devised a method for the quantitative estimation of the former colouring matter in indigo. The dye-stuff mixed with purified sand is introduced into a glass tube (25 × 90 mm. approx.) closed at one end with calico, which is placed in a Soxhlet apparatus, and the material extracted with pyridine. The pyridine extract is evaporated finally with the addition of hot water, and the precipitate, which consists of indirubin and a little indigotin together with impurities, is collected on asbestos, washed with dilute hydrochloric acid, to remove mineral matter, with 1 per cent alkali to dissolve indigo-brown, and finally with 1 per cent acetic acid solution. The crystalline residue is dried, sulphonated, and the solution of the mixed sulphonic acids analysed by means of the Duboscq colorimeter.

The residual mixture of sand and crude indigotin is washed in the Soxhlet apparatus with hot 10 per cent sulphuric acid, which removes indigo gluten and some mineral matter, and with water until free from acid; the residue is then dried and sulphonated in the ordinary manner, the product dissolved in water, the solution filtered, and titrated with permanganate or titanium trichloride. The accuracy of the process has been determined by an examination of mixtures of pure indigotin and indirubin, and the reliability of the colorimetric work, in respect of the amount of colouring matter present, by means of titanium chloride. The authors have also analysed certain special varieties of Java indigo and other indigos, and it was further pointed out that by this pyridine method a quantitative determination of indigo-brown is also possible.

DISCUSSION.

Mr. A. G. PERKIN said that although the fact that dilute solutions of the indigotinsulphonic acids were decolorised by less permanganate than that required for the isatin reaction had been known for some time, the matter had not as yet been investigated. It was therefore apparent that the oxidation took place in two stages, and there was some possibility that the sulphonic acid of Kalb's (*Ber.*, 1909, xlii., 3642) dehydroindigotin might be produced in this manner. More striking in this respect were the sulphonic acids of indirubin, because under similar conditions the quantity of permanganate necessary for decolorisation was approximately only 75 per cent of that calculated on the isatin equation. The primary product in the latter case was thus fairly stable in the presence of the oxidising agent, and attempts were being made to isolate it in the unsulphonated condition by the oxidation of indirubin itself.

178. "*The Colour and Constitution of the Amino-coumarins.*" By ARTHUR CLAYTON.

The colour of the amino-derivatives of coumarin and its homologues was shown to be independent of the position of the amino-group, and not to be due to the presence of a mobile hydrogen atom. The suggestion was made that the colour is generated by the continual breaking and reforming of valency bonds between the amino-group and the unsaturated ·O·CO· group present in the lactonic ring.

179. "*Estimation of Sodium and Cæsium as Bismuthi-nitrites.* Part I. *Estimation of Sodium.*" By WALTER CRAVEN BALL.

Sodium may be estimated even in the presence of a very large excess of potassium, by precipitation as sodium cæsium bismuthi-nitrite (*Trans.*, 1909, xcv., 2126). The precipitation is conducted in a special form of vessel, and the precipitate dried at 100° and weighed. The sodium present in complex mixtures, such as sea-water, may thus be estimated.

180. "*The By-products of Alcoholic Fermentation.*" By OLIVE EVELINE ASHDOWN and JOHN THEODORE HEWITT.

Alcohol as obtained by the fermentation of dextrose or dextrose-yielding materials by yeast contains numerous by-products. In certain cases these may be referred to substances other than dextrose, but acetic acid is probably furnished by the oxidation of acetaldehyde, which, in turn, is certainly derived from dextrose, since it is produced when pure specimens of this sugar are fermented in the presence of suitable nourishment, no other organic material being added.

The idea that the quantity of aldehyde might depend on the available nitrogen proved unfounded; incidentally, support is afforded to Ehrlich's view as to the source of the higher alcohols by the observation that addition of alanine diminishes the amount of these substances.

The amount of aldehyde may be diminished by the addition of small amounts of formates, a result of considerable interest in view of the statement of Schade (*Zeit. Phys. Chem.*, 1906, lvii., 1; 1907, lx., 510) that dextrose yields acetaldehyde and a formate under the influence of alkali, whilst acetaldehyde and formic acid yield ethyl alcohol and carbon dioxide with rhodium sponge as a catalyst.

181. "*Dimethoxyphenyl-p-tolylmethane.*" (Preliminary Note). By JOHN EDWIN MACKENZIE.

In previous communications (*Trans.*, 1896, lxix., 985; 1901, lxxix., 1204; 1904, lxxxv., 790; Clough, 1906, lxxxix., 771) the author and his collaborators have described the products formed by the interaction of benzophenone chloride and of benzylidene chloride on the sodium compounds of various alcohols and phenols.

It was thought that from phenyl *p*-tolyl ketone chloride a series of derivatives might be obtained according to the general equation—

$$C_6H_4Me\cdot CCl_2\cdot C_6H_5 + 2NaOR = C_6H_4Me\cdot C(OR)_2\cdot C_6H_5 + 2NaCl,$$

where R represents an alkyl group. A comparison of the physical properties of such compounds with those of the corresponding derivatives already obtained from benzophenone chloride and those to be obtained from ditolyl ketone chloride should prove interesting as showing the influence of the methyl group as a substituent of hydrogen in various positions.

Phenyl *p*-tolyl ketone was prepared by the action of benzoyl chloride on a large excess of toluene in presence of aluminium chloride according to Bourget's method (*Bull. Soc. Chim.*, 1896, [3], xv., 945). The ketone distilled between 184° and 191°/20 mm., and crystallised out on cooling. By re-crystallisation from alcohol, colourless crystals melting at 56—57° were obtained, the weight of crystals being 43 per cent of that theoretically obtainable.

The dichloride is formed by the action of phosphorus pentachloride on the ketone,—

$$CH_3\cdot C_6H_4\cdot COPh + PCl_5 = CH_3\cdot C_6H_4\cdot CCl_2Ph + POCl_3.$$

Overton (*Ber.*, 1893, xxvi., 26) appears to have obtained the crude chloride. As it decomposes very readily on heating, the following method of preparation was adopted:—To the ketone dissolved in ten times its weight of carbon tetrachloride, the equivalent weight of phosphorus pentachloride was added, and the mixture was then heated in a water-bath for four hours. The solvent was distilled off under 25 mm. pressure, the temperature being eventually raised to 85°. The residual dark green oil had a strong odour of hydrogen chloride, and was very unstable in presence of water, being re-converted into the ketone.

Determinations of chlorine made at the stated intervals gave the following percentages:—After one day 27·4 (theory 28·28), five days 15·35, ten days 7·8, eleven days 5·4, and on the thirteenth day crystals of the ketone separated out.

Dimethoxy-p-tolylphenylmethane was prepared by mixing the chloride with an equivalent weight of sodium methoxide in ten times its weight of methyl alcohol. A vigorous reaction took place. After filtering off the salt, the alcohol was distilled off under diminished pressure, and the residue extracted several times with ether. This ethereal solution was dried, the ether distilled off under the ordinary pressure, and the residue under a pressure of 15 mm. A colourless oil amounting to 77 per cent of the theoretical amount passed over between 163° and 165°. (Found, C = 79·8, H = 7·09; calc., C = 79·33, H = 7·44 per cent. M.W. by cryoscopic method = 249; calc. 242; density, 1·075 at 15°).

The following boiling-points were determined:—186°/26 mm., 312°/80 mm.

Efforts to obtain this substance in a crystalline form were in vain, the oil only becoming more viscous. It is easily miscible with the ordinary organic solvents.

As in the case of the corresponding benzophenone derivative, this substance when placed in a desiccator con-

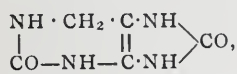
taining sulphuric acid steadily lost weight until the ketone crystallised out, the change being expressed thus:—

$C_6H_4Me{\cdot}C(OMe)_2{\cdot}C_6H_5 \rightarrow C_6H_4Me{\cdot}CO{\cdot}C_6H_5 + (CH_3)_2O$.

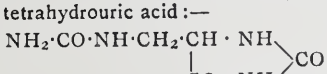
Experiments with ethyl and benzyl alcohols and with phenols are in progress.

182. "*A Synthesis of Tetrahydrouric Acid.*" By Edward Percy Frankland.

An attempt to synthesise the hypothetical desoxyuric acid,—



by the addition of cyanic acid to α3-diaminopropionic acid, $NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$, followed by the dehydration of the diurea derivative thus formed, led to the production of tetrahydrouric acid:—



or—

only one molecule of water being eliminated to form a hydantoin ring.

The product from the interaction of two molecules of potassium cyanate and one molecule of diaminopropionic acid in the presence of the equivalent quantity of either hydrochloric or hydrobromic acid was evaporated with 25 per cent hydrochloric acid, the resulting tetrahydrouric acid extracted with methyl alcohol and re-crystallised from water. It melts and decomposes at 216° (uncorr.), corresponding with the substance obtained by Tafel (*Ber.*, 1901, xxxiv., 258) by the electrolytic reduction of uric acid.

183. "*The Double Nitrites of Mercury and the Bases of the Tetra-alkylammonium Series.*" By Prafulla Chandra Ray.

The investigation on the double nitrites of mercury and the alkali metals and the metals of the alkaline earths (*Trans.*, 1907, xci., 2031; 1910, xcvii., 326) has been extended to the tetra-alkylammonium series. It is well known that the tetra-alkylammonium hydroxides are fairly comparable to the alkali hydroxides in point of strength, the heat of neutralisation of any one of these bases by an equivalent of hydrochloric acid being, on an average, 13,700 calories. It was therefore expected that the nitrites of the alkylammonium series should also yield double salts with mercuric nitrite, and this has been found to be the case.

In the interaction of mercuric nitrite and tetramethylammonium nitrite two distinct compounds were obtained, namely, $Hg(NO_2)_2{,}NMe_4NO_2{,}H_2O$ and $Hg(NO_2)_2{,}2NMe_4NO_2$. The power of combination of mercuric nitrite with one or more molecules of the alkali nitrite evidently depends on the predominance of the latter in solution.

(*Note.*—Although the salt $Hg(NO_2)_2{,}1\frac{1}{2}NaNO_2$ (*loc. cit.*) has been described, the corresponding mercuric potassium compound has not until now been obtained. The author has succeeded in preparing it in a pure state. Analysis of the salt gave:—Found: Hg = 47·72; K = 13·98; N = 11·60: $Hg(NO_2)_2{,}1\frac{1}{2}KNO_2$ requires Hg = 47·66; K = 13·98; N = 11 68 per cent).

Analysis of the compound $Hg(NO_2)_2{,}NMe_4NO_2{,}H_2O$ gave:—

Found: Hg = 44·64; C = 10·71; N (nitritic) = 9·37. $Hg(NO_2)_2{,}NMe_4NO_2H_2O$ requires Hg = 45·00; C = 10·63; N (nitritic) = 10·2 per cent.

The compound $Hg(NO_2)_2{,}2NMe_4NO_2$ gave:—

Found: Hg = 38·2; C = 17·7; N (total) = 16·1. $Hg(NO_2)_2{,}2NMe_4NO_2$ requires Hg = 37·6; C = 18·0; N = 15·8 per cent.

184. "*Ionisation of the Nitrites as Measured by the Cryoscopic Method.*" (Preliminary Note). By Prafulla Chandra Ray and Satish Chandra Mukherjee.

The authors gave a preliminary account of their work on the ionisation of the nitrites. This part was carried out in the ordinary way, and the results checked by comparison experiments with potassium nitrate and chloride and sodium chloride. The nitrites were prepared either from silver nitrite or barium nitrite, and treatment with the corresponding chloride or sulphate and evaporation to dryness in a vacuum over sulphuric acid. Instead of weighing these salts directly (as many were deliquescent), the authors evaporated the solutions (after the determinations had been made) with sulphuric acid and estimated the strength from the sulphate left. An exception to this was in the case of the tetramethylammonium nitrite, which was dried at 150° and weighed directly.

Salt.	Mol. wt. Calc.	Mol. wt. Found.	Dilution in litres.	Degree of ionisation.	No. of ions.
KNO_3	101·0	56·05	4·4	0·80	2
		54·37	19·0	0·86	2
KCl	74·5	38·2	15·0	0·95	2
		39·7	12·0	0·88	2
NaCl	58·5	31·4	4·2	0·86	2
$Ca(NO_2)_2$	132·0	49·3	28·0	0·84	3
		50·26	19·4	0·82	3
$Ba(NO_2)_2$	229·0	84·9	21·0	0·84	3
		84·0	31·4	0·86	3
$Sr(NO_2)_2$	179·3	66·43	22·0	0·84	3
		66·5	21·0	0·84	3
KNO_2	85·0	45·6	16·0	0·86	2
		46·0	17·0	0·85	2
		46·0	18·0	0·85	2
		44·4	36·0	0·91	2
$NaNO_2$	69·0	36·9	10·0	0·87	2
		36·0	20·5	0·91	2
NH_4NO_2	64·0	35·3	18·0	0·81	2
		34·2	20·0	0·87	2
$N(CH_3)_4NO_2$	120·0	63·0	14·0	0·90	2
		62·0	19·5	0·93	2
$HgCl_2$	271·0	258·6	36·6	0·47	3
$Hg(NO_2)_2$	292·0	238·2	32·0	0·11	3
$K_4Fe(CN)_6$	368·0	104·5	31·0	0·63	5
$Hg(NO_2)_2{,}2KNO_2$	462·0	131·4	7·2	[1·26]	3
		122·2	21·2	[1·39]	3
		110·65	60·4	[1·58]	3
$2Hg(NO_2)_2{,}3KNO_2$	839·0	154·0	23·0	[1·48]	3
$Hg(NO_2)_2{,}2N(CH_3)_4NO_2$	532·0	134·0	40·0	[1·48]	3
$Hg(NO_2)_2{,}Ca(NO_2)_2$	424·0	148·3	42·1	[1·86]	2
$3Hg(NO_2)_2{,}2Ba(NO_2)_2$	1334·0	173·7	126·0	[3·34]	3
$2Hg(NO_2)_2{,}HgNO_2$	830·0	294·0	64·8	[1·82]	2
		290·8	72·7	[1·85]	2
		299·5	135·2	[1·77]	2

Anomalous results are given in square brackets.

It will be seen that potassium and sodium nitrites on the one hand, and calcium, strontium, and barium nitrites on the other, show equal degrees of ionisation; thus these nitrites conform to the general rule that salts which have an analogous constitution are ionised to the same extent in dilute solutions of equal concentration.

It is worthy of note, also, that a solution of ammonium nitrite—a compound of a "weak" base and a "weak" acid—shows no deviation from the general rule, and that a solution of tetramethylammonium nitrite is far more strongly dissociated than any of the alkali nitrites, a fact in keeping with the behaviour of other salts of quaternary bases from aliphatic amines.

The results are in agreement with those obtained by other investigators using different methods.

(To be continued).

NOTICES OF BOOKS.

Memorias do Instituto Oswaldo Cruz. ("Memoirs of the Oswaldo Cruz Institute"). Vol. I., Part II. Rio de Janeiro. 1909.

THE reports issued by the Oswaldo Cruz Institute at Rio de Janeiro merit the careful attention of bacteriologists, who will find that they contain the accounts of a large amount of important original work. The reports are printed both in Portuguese and English or German in parallel columns, and consist exclusively of papers on biological subjects, which are beautifully illustrated by coloured plates.

Die Theorie des Färbeprozesses. ("The Theory of Dyeing"). By L. PELET-JOLIVET. Dresden: Theodor Steinkopff. 1910.

THE theory of dyeing has taken a new aspect in the light of recent work on adsorption and contact electrification, but there still remains much to be done and many explanations to be found before the gaps in our knowledge can be satisfactorily bridged over. The first step towards the solution of the problem as it now stands is to define exactly the line of demarcation between the accurately known and the unknown, and the author of this book has set himself the formidable task of reviewing all that has been published on the theory of dyeing. On the whole he has acquitted himself very successfully. While not aiming at being exhaustive, the book indicates clearly the main advances which have been made recently, and gives copious references to the literature of the subject. The author expresses his belief that by the systematic study of adsorption compounds the solution of the problem of the nature of the process of dyeing will be found, provided that their relations to chemical compounds are accurately ascertained, while simultaneously our knowledge of the latter will be amplified, and possibly other problems of technical importance will be solved.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cl., No. 18, May 2, 1910.

Action of Silent Discharge on Chloroform and Carbon Tetrachloride in Presence of Hydrogen, and on Methyl Chloride.—A. Besson and L. Fournier.—The silent discharge converts chloroform into a series of products which may be regarded as the chlorinated derivatives of the hydrocarbons C_nH_{2n+2} and C_nH_{2n}, the former being obtained simply by abstraction of one or more molecules of hydrochloric acid. Methyl chloride gives two series of products—those belonging to the saturated series (chloride of ethylene) and homologues which differ by CHCl, and ethylenic derivatives which contain HCl less. Of the latter only one representative, $C_4H_5Cl_3 = C_4H_6Cl_4 - HCl$, has been isolated.

Isomerism of some Acetylenic-γ-Glycols.—G. Dupont.—The glycol $CCl_3-CHOH-C\equiv C-CHOH-CCl_3$, obtained by the action of chloral on dibromomagnesium acetylene, on fractional distillation in carbon tetrachloride, yields two isomers, one fusing at 135° and the other at 117—118°. Similarly $C_6H_5-CHOH-C\equiv C-CHOH-C_6H_5$ yields two isomers, and also—

$$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix} > COH-C\equiv C-COH < \begin{matrix} C_6H_5 \\ CH_3 \end{matrix}.$$

These isomers always appear to possess the same symmetrical formulæ, and hence they must be the stereochemical isomers, the existence of which is foretold theoretically.

Condensation of Secondary Amines with γ-Bromodimethylacetyl Acetic Ether.—H. Gault and G. Thirode.—The γ-bromodimethylacetyl acetic ether, prepared by the direct action of bromine on dimethylacetyl acetic ether, condenses normally with diethylamine and ethylaniline, giving the corresponding amine derivatives, *e.g.*, $(C_2H_5)_2N-CH_2-CO-C(CH_3)_2COOC_2H_5$.

Product of Methylation of Komppa's Diacetoapocamphoric Ether.—J. F. Thorpe and G. Blanc.—In 1903 Komppa announced that he had synthesised camphoric acid by the following reactions:—Methyl oxalate is condensed with ββ-dimethylglutaric ether, yielding methyldiacetoapocamphorate. The latter by methylation and reduction is converted into camphoric acid. The authors have, however, repeated the process, following Komppa's directions, and have found that his diacetocamphoric ether cannot have the constitution he ascribed to it, but that it is a compound containing 9C, from which it is difficult to see how camphoric acid with C_{10} could be produced.

Hydrogenation of Essence of Terebenthene.—G. Vavon.—The author has investigated the products of the hydrogenation of the fractions of essence of terebenthene, which distil over between 155° and 165°. He finds that the only constituents of these fractions are α- and β-pinene, which both give the same hydrocarbon. The hydrogenation of the *l*- and *d*-essence shows that β-*l*-pinene is present in large quantities in them.

Partial Hydrogenation of Acids of Stearolic Series.—A. Arnaud and S. Posternak.—Fatty acids of the series $C_nH_{2n-4}O_2$ can be converted into acids of the series $C_nH_{2n-2}O_2$ by the reduction of the monohydrogen iodide derivative by means of zinc. Thus stearolic acid can be converted into elaidic acid.

MISCELLANEOUS.

Free Places at the Imperial College of Science and Technology, 1910.—On December 21st, 1909, the London County Council decided to make a maintenance grant of £8000 to the Imperial College of Science and Technology, South Kensington. In return for this grant it secures the privilege of nominating twenty-five students for one year's free instruction at the Imperial College. These are now to be filled for the first time. The instruction will be of an advanced nature, and therefore only advanced students who are qualified to enter on the fourth year of the course should apply. There is no restriction as to income, but intending candidates must be ordinarily resident in the Administrative County of London, and must be students at an institution aided, maintained, or approved by the Council. The free studentships do not entitle the holders to any maintenance grants, but cover all ordinary tuition fees. No examination will be adopted for the final selection of the students from the applications received. The free studentships will be awarded on consideration of the past records of the candidates, the recommendations of their teachers, the course of study they intend to follow, and generally upon their fitness for advanced study in science applied to industry. It is quite possible that, in special cases, the free places may be extended to two or more years. Application should be made without delay, as entries will not be considered after July 23rd, 1910. Application forms (T.2/268) can be obtained from the Education Officer, London County Council, Victoria Embankment, London, W.C.

THE CHEMICAL NEWS.

VOL. CII., No. 2643.

THE DECOMPOSITION OF YTTERBIUM.*

By C. AUER v. WELSBACH.

IN view of the persistence with which G. Urbain endeavours to lay claim to priority in the discovery of the ytterbium elements, and of the effects of his assertions on the minds of some of my colleagues, I feel obliged to open up this question once more, and to explain thoroughly the true state of affairs, as shown by the articles which have been published on the subject.

At the beginning of the year 1905 I discovered that ytterbium could be split up. Some months later I reported this discovery to the Kaiserl. Akademie der Wissenschaften in Vienna. This report was put before the meeting of the Mathematical and Scientific Section on March 30, 1905, and appeared in the Akademie's *Anzeiger*, 1905, No. 10.

In this report I showed that ytterbium consists essentially of two elements, the spark spectra of which are parts of the ytterbium spectrum. I pointed out that some lines appear to be common to both spectra.

This report is reprinted word for word in Appendix I.

In the middle of 1906 I published an article "On the Elements of the Yttrium Group" (Part I.) (*Sitzungsber. d. Kaiserl. Akad. d. Wissensch. in Wien.*, cxv., Part II. B, July, 1906), in which I described the results which I had obtained in the separation by fractional crystallisation of the double ammonium oxalates of the yttrium elements.

In this article I laid stress on the conclusion that the spark spectrum of the head fraction of the ytterbium series, when compared with the ordinary ytterbium spectrum, showed very striking differences (see Appendix II.).

I also discussed the decomposition of ytterbium in an article which appeared in 1906, "Notes on the Use of the Spark Spectrum as a Test of Homogeneity" (*Festshrift Adolf Lieben und Liebig's Annalen der Chemie.*, vol. cccli.). On p. 464 of this article I said:—

"During the investigation of the ytterbium ammonium oxalates I noticed peculiar phenomena which suggested that ytterbium is not an elementary substance. I first compared the different fractions with one another and with pure ytterbium which I had previously prepared, but in spite of the most careful comparison I could find no proof of the correctness of my conjecture. Nevertheless, I continued the fractionation. After a long time I got a preparation which with a faint spark showed very distinct differences of intensity in some lines in the red which are characteristic of ytterbium when compared with other ytterbium preparations. As the separation process was continued these differences became gradually more marked. Some lines in the red began to get pale, while others became more bright. Then the changes in the brightness of the lines began to become visible in other parts of the spectrum as well.

When after continuing the separation process for a long time I compared the ytterbium fractions which were furthest distant from one another, the great differences between the two spectra appeared very clearly. By continuing the decomposition process I finally reached a point at which the purest preparations, even with a strong spark, had no longer any lines in common in the optical part of the spectrum.

I now photographed the spectra obtained with a concave grating in absolutely comparable experimental conditions in the region from λ 4500—2600. The perfectly clear negatives, which showed very strong contrasts, when directly compared, formed an interesting picture. Almost all lines were as fine as hairs when moderately magnified. Only a few were much broadened and somewhat indistinct towards the edges in consequence of the formation of light halos, and were often accompanied by ghosts. The strongest platinum lines and some calcium lines appeared in both spectra as fine lines. On the whole the two spectra were very different from one another, although apparently they had some very strongly marked lines in common. The strongest lines of one spectrum were present as faint lines in the other, and the shorter their wave-lengths the clearer they were.

Thus, while in the region of longer wave-lengths λ 7000–5000 on ocular examination the two spectra appeared totally different; this difference was much less apparent in the photograph of the ultra-violet part, apart from the common lines."

By these definite experiments the scientifically rigid proof of the decomposition of ytterbium into two new substances was established. This seems to me to be quite enough to prove the truth about the priority. I will therefore forbear to add to my previous communications any further details on the wave-lengths or the atomic weights. As regards the latter I may mention that I had already communicated them in the year 1906 to anyone who asked for them. Thus I repeatedly gave for the one constituent of ytterbium—cassiopeïum—the value Cp = 174·28, and for the other—aldebaranium—the value Ad = 172·52. Moreover, it may be pointed out that at that time I made no secret of my work; both I and my assistants willingly gave full information concerning the new substances to any one who asked for it (*Zeit. Anorg. Chem.*, 1909, lxiv., 119).

Finally, it may be mentioned that in the article quoted above, the beginning and the course of the separation processes were described. For those who wished to make use of the new methods of separation this was of inestimable value.

On the basis of my experiments I can say that in the given conditions, if no time were wasted in useless methods of separation, no chemist who was provided with the necessary materials would have had any difficulty in purifying within a period of about six months the decomposition products of ytterbium to such a degree that he could easily recognise the changes of intensity of the lines of the spark spectra, and could pick out the chief lines belonging to the separate substances.

After all that I had reported on the decomposition of ytterbium I was justified in assuming that the necessary time would be allowed me to work out thoroughly this discovery, which had been made after endless trouble and at great cost.

A year after my last publication this tedious work was concluded, and at the end of 1907 the article, which had become fairly comprehensive, was ready for press.

Then, at the beginning of November, G. Urbain published his first notice, "A New Element, Lutecium, obtained by the Decomposition of Marignac's Ytterbium" (*Comptes Rendus*, cxlv., 759),

The most important points in this article are reproduced in Appendix III.

This article, which was not by any means conclusive, bore evident traces of haste.

Definite atomic weights were not given. "The atomic weight of neo-ytterbium cannot differ much from 170, and the atomic weight of lutecium is not much above 174." This is an inadequate statement for the ytterbium elements, especially when it is noted that the atomic weight of ytterbium = 173·0, while that of the second constituent of ytterbium—aldebaranium— is 172·90.

It is evident from Urbain's statements and measurements of the spark spectra that his fractions, at the time of his first publications, were still very impure. He says:—"Apart from these lines (thulium lines) the two spectra showed a great number of common lines of equal order of intensity. These lines are those which characterise the bulk of the original material, the impurities of which (thulium and a new element) accumulated, the former in the first and the latter in the last of my fractions."

* *Sitzungsber. d. Kaiserl. Akad. der Wissensch. in Wien.*, Math.-Sc. Section, vol. cxviii., Part II. *b*, October, 1909.

He then says, under 2:—"The following lines are the characteristic lines of the new element. For the limits between which my measurements extend these 34 lines constitute the relatively complete spark spectrum of the new element."

We will examine into these statements rather more closely. Firstly, I must point out that five of these lines are not in my photographs of the spectrum of cassiopeïum. They are the following:—2798·3, 3080·3, 3183·5, 3275·5, and 3506·8. One of these lines, viz., 2798·3, belongs to aldebaranium; 3080·3 and 3506·8 must be thorium lines (see F. Exner and E. Haschek's "Wave-length Tables").

It must also be pointed out that of the 34 lines which, according to Urbain, are characteristic of the "new element," the strong and characteristic lines 2796·75, 3279·15, 3281·87, and 3507·56, are missing. This is all the more striking because Urbain has not omitted to include on his list those lines which are only numbered among the very faint lines of the cassiopeïum spectrum.

Urbain also mentions the bands of the spark spectrum. He says that the band (λ517·5—513) must belong to the new element. This is not correct, for this cassiopeïum band can easily be traced to 520.

The band λ 466—472·5 in the blue, the most characteristic and finest of the cassiopeïum spectrum, is not mentioned. Thus Urbain's statements cannot be used for the identification of the spectrum of cassiopeïum.

It is evident from the foregoing that Urbain at the time of his first publication had not actually succeeded in decomposing ytterbium. For this reason there was no warrant for giving new names and symbols to the very impure decomposition products which naturally failed to give him any proof of homogeneity.

His remark at the end: "Herr Auer v. Welsbach has quite recently announced that by the fractionation of the double oxalates of ammonium and ytterbium he has detected spectral variations which he has not further defined. He did not give any measurements of the lines which he observed between λ 7000 and λ 5000, and did not separate the elements which he supposes to exist in the old ytterbium" is obviously disproved by the above statements.

A few days after I heard of the appearance of Urbain's notice I sent my article to the Kaiserl. Akademie der Wissenschaften in Vienna, under the title already used in 1905, "The Decomposition of Ytterbium into its Elements" (*Sitzungsber. d. K. Akad. der Wissensch. in Wien.*, vol. cxvi., Part II. B, December, 1907).

This article follows directly on my paper "On the Elements of the Yttrium Group," and confirms all the statements that I had made in my earlier publications. It contains the atomic weight determinations, the wave-length tables, and the accurate spectrograms, magnified by the silver bromide process, of the new elements for the region from 6130 to 2570.

Some of the most important points in this article are given in Appendix IV.

In order to make this work accessible to a larger circle, I will willingly send it to any colleague on request—as long as my stock lasts.

Urbain has published a further communication on the ytterbium elements which, however, I need not further refer to, as it is not of importance either as regards the question of priority or otherwise.

I may mention that in his second publication, which was sent in February, 1908, to the Académie in Paris, in speaking of my article mentioned above, which was not issued till May, 1908, he unfortunately gave my atomic weights partially incorrectly, and also affirmed that I had contented myself with saying that differences in their spectra (the ytterbium elements) existed, without further defining them. Then he states that aldebaranium is undoubtedly identical with lutecium and cassiopeïum with neo-ytterbium. To be correct this statement should run:—Cassiopeïum has not much to do with lutecium, and aldebaranium nothing whatever to do with neo-ytterbium.

Appendices

To the article "The Decomposition of Ytterbium," by C. Auer von Welsbach, in the *Sitzungsber. d. Math. Wissensch. Klasse d. K. Akad. der Wissensch*, 1909, vol. cxviii., II. B, p. 507, and *Monatshefte f. Chem.*, 1909, vol. xxx., p. 695).

Appendix I.

(*Anzeiger d. Math. Naturwissensch. Klasse d. K. Akad. d. Wissensch.*, 1905, No. 10. By C. Auer v. Welsbach).

"In the course of experiments with the rare earths which I have been carrying out for some years, I recently succeeded in proving that ytterbium, which was discovered by Marignac in 1878, and of which the elementary nature appeared doubtful, judging from spectral observations, is actually a compound substance (see Exner and Haschek, *Sitzungsber. d. K. Akad. d. Wissensch. in Wien, Math.-wissensch. Kl.*, cvii., II. A). It consists essentially of two elements.

If the right method of separation is chosen the two new elements can be purified comparatively easily.

The spark spectra of the new elements are parts of the ytterbium spectrum, and the the latter may be regarded as the sum of the two new spectra.

Some lines appear to be common to both spectra.

The salts of the ytterbium elements are colourless, and by themselves produce no absorption in the visible part of the spectrum.

But they exert a remarkable influence on the absorptive power of the salts of chemically allied elements. Thus if they are present in considerable quantity they completely change the spectrum of erbium; characteristic lines and bands are extinguished, and new appear in their places. This power of producing variations, which, moreover, is in a different degree peculiar to the new elements, also extends to the spectra of the incandescent earths."

Appendix II.

(*Sitzungsber. d. Math. Naturwissensch. Klasse d. K. Akad. d. Wissensch.*, 1906, vol. cxv., II. B, p. 11. By C. Auer von Welsbach).

"After the separation of the thorium I again dissolved the oxalates of the earths in ammoniacal ammonium oxalate solution, filtered off the silica which had remained undissolved, and carefully fractionated the solution to a small residue. This should now contain the purest ytterbium. But the spectral examination showed that this was not the case, for the spark spectrum, which contained no lines of foreign substances, showed very striking differences when compared with the ordinary ytterbium spectrum. These are the first indications of the possibility of decomposing ytterbium.

I have omitted to give descriptions of the different spectra in this article, because I shall return to all the characteristic spectra in the special article mentioned at the beginning."

Appendix III.

(*Comptes Rendus*, 1907, vol. cxlv., p. 759. By G. Urbain).

By the arc spectra method I was not able to detect the presence of any impurity in my products which had been thus purified, and there was no doubt that my ytterbia was a mixture of several constituents.

By photographing on the same plate one above the other the arc spectra of the extreme members of this fractionation, I detected in the spectrum of the last fraction (No. 31) many lines, mostly well marked, which could not be seen in the first fraction (No. 17), or which were only very faint in it. Conversely, Fraction 17 showed some not very strong lines which were absent in 31, and were probably attributable to thulium. Apart from these lines the two spectra showed a great number of common lines of the same order of intensity. These lines are those which characterise the bulk of the original material, the impurities in which (thulium and the new element) accumulated, the former in the first and the latter in the last of my fractions.

I then compared the spark spectra of my earths. The differences detected by this method of observation were much clearer than in the case of the arc spectra.

1. The following lines are the spark lines due to thulium, which I detected in the fractions of low atomic weight (least soluble nitrates) :—

2869·3 Faint	3362·7 Fairly strong
2899·9 Medium	3425·7 „
2962·5 „	3441·6 „
3050·9 Faint	3461·9 „
3131·4 Fairly strong	3624·5 Faint
3151·2 Medium	3712·5 „
3173·0 „	

2. The following are the lines which are characteristic of the new element. They may very easily be seen in the fractions of high atomic weight (most soluble nitrates). They are either found exclusively in these fractions or are much strengthened in them.

*2701·8 Very strong	3171·5 Fairly strong
*2754·2 „	*3183·5 Medium
*2798·3 „	3191·9 „
*2847·6 „	*3198·2 Strong
2895·0 „	*3254·5 Very strong
*2900·4 „	3275·5 Fairly strong
*2911·5 „	*3312·4 Strong
*2951·8 „	*3359·8 „
*2963·5 „	*3376·7 „
2970·0 „	*3385·6 Fairly strong
*2989·4 Medium	*3397·2 Very strong
3020·7 Very strong	*3472·6 „
*3056·8 „	*3506·8 „
3058·0 „	3554·6 „
*3077·7 „	3568·0 Strong
*3080·3 Medium	3624·1 „
3118·6 „	3647·9 „

The lines marked with asterisk are the most characteristic lines of the arc spectrum.

For the limits between which my measurements extend, these thirty-four lines constitute the relatively complete spark spectrum of the new element. (None of these lines is due to scandium, thorium, erbium, thulium, yttrium, or to any other element or rare earth, except the old ytterbium).

I propose the name lutecium, Lu, derived from the old name of Paris, for the name of this element.

3. The other lines, included within the same limits and enumerated in the spark spectrum of ytterbium recently described by Sir William Crookes from one of my old preparations (*loc. cit.*), characterise the bulk of the old ytterbium. I propose to give this earth the name neo-ytterbium, Ny, in order to avoid confusion with Marignac's element.

4. The first spectrum of the old ytterbium was described by Lecoq de Boisbaudran (*Comptes Rendus*, 1879, lxxxviii., 1342), to whom Marignac had sent his new earth. It was a band spectrum. When I examined the chlorides of the extreme members of my fractionation by Lecoq de Boisbaudran's method I noticed that in the earths of low atomic weight (neo-ytterbium) Lecoq de Boisbaudran's band γ was absent. On the other hand, in the earths of high atomic weight, which are very rich in lutecium, this band γ is more marked than the other bands of the spectrum.

The bands α (from $\lambda = 559$ to $\lambda = 552$) and β (from $\lambda = 576$ to $\lambda = 568{\cdot}5$) are thus probably characteristic of neo-ytterbium, and the band γ (from $\lambda = 517{\cdot}5$ to $\lambda = 513$) of lutecium.

To summarise the preceding observations, Marignac's ytterbium is a mixture of two elements, neo-ytterbium and lutecium. The atomic weight of neo-ytterbium cannot differ much from 170, and the atomic weight of lutecium is not much above 174.

Moreover, Auer v. Welsbach (*Lieb. Ann.*, 1907, cccli., 464) has quite recently announced that, by the fractionation of the double oxalate of ammonium and ytterbium, he has detected spectral variations which he has not further defined. He did not give any measurement of the lines which he observed between λ 7000 and λ 5000, and did not in any way specify the elements which he supposes exist in the old ytterbium."

Appendix IV.

(*Sitzungsber. d. Math. Naturwissensch. Klasse d. K. Akademie d. Wissensch.*, 1907, cxvi., II. B, p. 11. By C. Auer von Welsbach).

"As may be seen from the following description of the spark spectrum of the two new elements, neither Yb I. nor Yb II. appears to be capable of being further decomposed by any means at present at our disposal.

As the decomposition of ytterbium into two new elements has been proved experimentally beyond doubt, it will be best to use the name ytterbium for the future only as a collective name, and to give new names to the new substances. I suggest the name—

Aldebaranium (symbol Ad) for the element called in the first part of this article Yb II., and resembling thulium or erbium, and—

Cassiopeïum (symbol Cp) for the second element, called Yb I. in this article, the last in the series of the rare earths."

The Atomic Weights.

Page 12. "The atomic weights of the elements are very close.

Determinations performed according to Bunsen's method gave for aldebaranium—

Analysis.	Oxide.	Sulphate.	
I.	0·4181	0·6730	172·98
II.	0·5984	0·9634	172·88
III.	0·6173	0·9939	172·85
Mean for aldebaranium			172·90

For cassiopeïum—

I.	0·3716	0·5967	174·25
II.	0·3086	0·4956	174·19
III.	0·4026	0·6465	174·24
Mean for cassiopeïum			174 23

The following notes on these determinations may be added :—

The oxide of Analysis I. of aldebaranium was derived from an oxalate which had been obtained by repeated precipitation from a solution made strongly acid with nitric acid.

The oxides of Analyses II. and III. of Ad and the oxides of the analyses of Cp were repeatedly precipitated with ammonia free from CO_2, from a nitrate solution free from CO_2 and containing much ammonium nitrate.

The accuracy of the atomic weight determinations of these elements, apart from the magnitude of the atomic weights, is unfavourably affected by the fact that the sulphates of these elements are less stable on ignition than the sulphates of the other rare earths."

Page 13. "The spark spectra of the two new elements are relatively poor in lines, but they belong to the brightest known. This holds good especially for cassiopeïum. The few lines which this substance possesses in the optical part of the spectrum recall the magnificent barium spectrum. Besides these lines, the Cp spectrum is characterised by two channelled bright bands in the green and blue, somewhat recalling the Cy spectrum. While the band in the green consists of several fine lines, that in the blue is of a nebulous character. With the dispersion which my apparatus possesses the resolution into lines could not be effected. The light maxima lie towards the refrangible part of the specrum ; thus the structure is the opposite of that of the Cy bands.

The spectrum of Ad is much richer in lines than that of Cp, both in the optical and ultra-violet parts. Most of the Yb lines occur in it."

Page 23. "Several lines, especially in the ultra-violet, occur in all three spectra with the same intensity. I have marked them *g.l.* in the table, *i.e.*, common lines.

It is not probable that these are only apparent coincidences. For this peculiar phenomenon appears with all elements which are closely allied chemically, *e.g.*, neodymium and praseodymium.

Finally, I have still to mention a third group of lines which are strongest in the spectra of the middle fractions; they appear specially clearly on the sensitised plates after a long time of illumination (600 seconds).

To these belong the lines 5104·60, 5067·40, 5009·72, which in the spectra of Ad and Cp show no corresponding marked lines. All these lines indicate that between Ad and Cp a third Yb element exists, if in small quantities only. Unfortunately it is hopeless to try to get this element even in a half pure state; for the separation processes, even supposing that the tendency to separate remained the same, which is not certain, would take many years."

THE FRUIT OF *MENISPERMUM CANADENSE*.

By RAY E. NEIDIG.

THE fruit of *Menispermum canadense*, or more commonly called "moon seeds," was gathered from a vine growing beside a porch on a residence in Mount Vernon, Iowa, November 13th, 1909. The vine grows to a height of about 12 feet. The berries ripen in September, and when ripe look like frosted grapes. The berries are a bluish black colour, and when dried they resemble commercial currants in shape, but about twice the size. The berries have but one seed, which is crescent shape. The odour and the taste of the berries are similar in both respects to raisins. The weight of a berry is 0·3017 grm.

The taste on first putting into the mouth is sweetish, which quickly passes to a bitter sweet similar to that of the bark of a peach tree. On burning the fruit a pleasant smell similar to that of cooked sorghum first passes off; then an odour of burnt coffee, and, lastly, a sharp penetrating odour resembling the burning of green or damp leaves. The fruits were easily crushed, and when ground fine a sticky mass resulted, indicating a considerable amount of sugars in the berries.

The Sugars.

About 50 grms. of the berries were taken for the sugar extraction. They were placed in a 500 cc. flask fitted with an inverted condenser, and treated with alcohol for 200 hours. The alcoholic extract was removed every twenty-four hours, and a fresh portion supplied. This alcoholic extract, which resembled burnt sorghum, was distilled. There remained behind a dark thick syrup. A test with Fehling's solution after 200 hours showed the sugars to be almost extracted, so distilled water was substituted for the alcohol. The berries while treated with alcohol remained hard, but on the addition of water they became soft and mushy. The alcoholic extraction at the end of 200 hours was almost colourless, but on the addition of water the extract became almost black in colour. The berries were boiled in water another 200 hours before all the sugar was removed.

The two different solutions were evaporated; the first to 500 cc. and the second 1000 cc. bulk. They were then treated with Fehling's solution of standard strength, 1 cc. corresponding to 0·005 grm. sugar. One cm. of the alcoholic solution reduced 21·2 cc. Fehling solution. The 1 cc. was placed into 50 cc. of distilled water and boiled. The Fehling solution was then added drop by drop. To ascertain when the end-point was reached a small portion of the solution was filtered from time to time, always pouring the filtrate back until the sugar had no more reducing power. The filtrate was a marked straw colour until the reduction was complete, then it changed to a light blue. There was found to be 53 per cent of sugar in the alcoholic solution, $21{\cdot}2 \times 500$ (which was the number of cc. of solution) $\times 0{\cdot}005 = 53$ per cent.

The water solution was treated the same way, 1 cc. reducing 1·6 Fehling's solution, so $1{\cdot}6 \times 1000$ (which equals the number of cc.) $\times 0{\cdot}005 = 8$ per cent. The total sugar was $53 + 8 = 61$ per cent. This corresponds closely to the loss in weight of the berries. There were 50 grms. to start with, and on drying after sugar was taken out we had 19 grms., showing a loss of 31 grms. or 60·2 per cent.

We purified 50 cc. of the alcoholic extract and water extract by the basic lead acetate method as described by Allen. The alcoholic extract was much easier to purify than the water extract. From the alcoholic extract we secured some beautiful sugar crystals. They were needle-like in shape, a few forming in clusters, and the rest were scattered. We failed to get crystals from the water solution. Judging from the time it took to extract the sugar from the water solution and the difficulty in purifying the same, the alcoholic treatment of extracting the sugar seems preferable.

A portion of the alcoholic solution was purified with bone-black by boiling several hours on the water-bath. The solution became quite clear after filtering, and the filtrate was used for testing different kinds of sugars. A portion of the extract and cobalt nitrate indicated dextrin very plainly. Another portion treated by Wohler's method (0·6 grm. sugar crystal dissolved in 10 cc. of 10 per cent ammonia solution) indicated maltose and lactose.

Millikin's method (0·2 grm. c.p. phenylhydrazin-hydrochloride, 0·1 grm. sugar crystals, 0·3 grm. sodium acetate, and 2 cc. of water) gave a precipitate in three and a-half minutes when placed in boiling water indicating glucose, so it is quite likely that all four are present, but glucose and dextrose predominate.

The Oils.

200 grms. of the berries were placed in a flask with an inverted condenser and the sugars removed by alcohol as before. Then the berries were dried, ground in a coffee mill, and placed in a flask with ether, and boiled under an inverted condenser for three weeks. The oil was removed from the ether by distillation. The oil was at first a beautiful green colour, due, no doubt, to chloro phyll. It was purified by heating thirty hours with ether and bone-black under an inverted condenser. When filtered the oil came out a beautiful pale amber colour with a greenish cast, the specific gravity of which was 0·96844. This is very nearly the specific gravity of castor oil as given by Allen, who places it between 0·958 and 0·970. The total amount of oil obtained after heating in the drying oven at 95° to 110° was 10·6746 grms., or about 5·38 per cent of the berry. The oil came, no doubt, from the seed, which is flat, moon-shaped, and containing a moon-shaped embryo from whence the berry gets its name.

A portion of the oil was taken to determine the saponification number by Koetlstorfer's process; 2·1821 grms. oil heated fifty hours gave a saponification equivalent of 326·17. This also indicates castor oil, Allen giving it between 302 and 319.

The soluble fatty acids were determined by Reichert's process, and the Reichert number obtained was 1·23. Allen gives 1·22 for 2·1821 grms. of oil. The results seem to indicate quite distinctly that the substance is castor oil.

The Ash before Removing the Sugars and Oils.

Five portions of the berries of exactly 2 grms. each were ashed in a platinum evaporating dish. From the first, silica, iron, alumina, calcium, and magnesium were determined.

From the second portion the sodium and potassium were removed by the J. Lawrence Smith method, from the third portion the sulphates, from the fourth the phosphates, and

lastly the manganese and chromium were determined by colorimetry. Two grms. were ashed, giving 0·695 grm. The ash was dissolved in 5 cc. concentrated HNO_3 in a test-tube, and 0·5 grm. of a saturated solution of $K_2S_2O_8$ and 0·5 cc. of a saturated solution of $AgNO_3$ added. The tube was filled to the 15 cc. mark with water. Five other tubes were prepared with HNO_3, $AgNO_3$, and $K_2S_2O_8$, and portions of a standard solution of $KMnO_4$ with a strength of 0·000158 to a cc. added to each tube. The one containing 0·73 cc. matched the tube with the ash. $\left[(0{\cdot}000158 \times 2{\cdot}3) \times \frac{55}{158}\right] \div 0{\cdot}0972 = 0{\cdot}041$ per cent manganese. The chromium was tried for by the same method, using instead a standard solution of $K_2Cr_2O_7$. I failed to detect chromium in the ash.

The analysis showed more potassium than sodium, and the flame test of the berry and sugar pointed in the same direction. The results of the analysis were as follows :—

	Per cent.
K_2O	52·65
Na_2O	15·09
Al_2O_3	2·34
Fe_2O_3	6·749
CaO	9·35
MgO	0·289
Mn	0·041
Chromium	—
P_2O_5	0·394
SO_3	6·12
CO_2	6·99
Total..	100·013

Five other portions were treated in the same way, and the results agreed very closely with the first. The average of the two ashings was 0·0783 for 2 grms. of the berries, or 3·91 per cent of the berries were ash.

After removing the sugar the same tests were applied as before, and the substances determined quantitatively. Two grms. of the substance were taken in each case, and the work was repeated in each case to ensure a more accurate result. The average of the ten ashings was 0·0695, or 3·47 per cent of the remaining substance was ash. The results were as follows :—

	Per cent.
K_2O	36·59
Na_2O	5·26
Al_2O_3	6·33
Fe_2O_3	5·32
CaO	20·00
MgO	5·69
Mn	0·181
Chromium	—
P_2O_5	4·13
SO_3	5·62
CO_2	9·389
Total..	98·528

The Proteins.

Some of the berries were crushed and boiled in distilled water for a short time. A small amount of the solution was heated with nitric acid. This gave a yellow colour, which changed to an orange-red when made alkaline.

The berries when heated with soda-lime, or when heated alone in a test-tube, gave strong fumes which reacted alkaline to litmus-paper.

The nitrogen was determined by the Kjeldahl method, 2 grms. of the berries yielding 0·95 nitrogen. The presence of sulphur was detected in the albumen by treating a solution of lead acetate with caustic soda until the precipitate which first forms re-dissolved. The fruit solution was now added and heated to boiling ; a dark precipitate of lead sulphide formed, which indicated sulphur. Millon's reagent also showed a test for albumen,

The Acids.

The acid tests were made from the sugar extract. The tests for the common organic acids were used which showed a very strong test for citric acid ; a small amount of oxalic was detected, also a trace of malic acid.

Gallic acid was shown to be present by the red precipitate obtained with ferric chloride and potassium cyanide.

Many thanks are due to Dr. Nicholas Knight for valuable suggestions which he offered during the work.

Cornell College, June 16, 1910.

MANUFACTURE OF ETHYL ALCOHOL FROM SAWDUST.

By G. U. BORDE, M.E.

I HAVE just returned from Europe where I went to investigate the manufacture of ethyl (grain, not wood) alcohol, acetic acid, and stock food out of sawdust.

In France I found that a company was organised, the aim of which was to control the entire output of the sawdust in France ; which, by the way, is only the equivalent of wood waste given out by one of our saw-mills having a capacity of 750,000 feet board measure per day.

One of the principal stockholders in this concern is the largest distiller and exporter of French cognac in France, and his object in obtaining control of this company was to have the exclusive right to the alcohol made from the sawdust so that he could use it in the rectification of brandy. He admitted that he exported to England alone 50 per cent more French cognac than the entire crop of France, and that he also sold to the balance of Europe and to the United States as well. Up to the present time he had been using alcohol made from beet-sugar for the rectification. Samples of the alcohol submitted to the experts in the alcohol exchange of Paris were declared to be equivalent, if not superior, to the alcohol distilled from grapes—so much for the quality of the product.

The process used is one discovered by Dr. Alexander Classen of the Polytechnic School of Aachen, Aix-la-Chapelle, Germany, in 1900. He found that he could convert the cellulose existing in all woody fibre into a fermentable sugar by cooking the wood under pressure in the presence of sulphurous acid, and then by fermenting the sugar thus formed, obtain ethyl alcohol. This process he patented all over the world ; but his original methods were crude, and the French people, after having purchased the patent rights for France, set to work to develop the process commercially. They changed the design of the apparatus suggested by Dr. Classen for the conversion, and further experimenting found that, in addition to the sugars formed, a considerable quantity of acetic acid was produced at the same time ; and so in their process they have made arrangements to extract the acetic acid as well as the alcohol.

At St. Marcel I found one of these plants in the course of construction, and the management kindly turned it over to me for experimenting. Twenty tons each of cypress shavings and long leaf yellow pine sawdust had been shipped from the South, and twenty tons of mixed hard woods from Chicago. While the plant was in course of construction enough of the apparatus was in place to carry the process through successfully, but enough was missing to prevent me from getting an absolutely accurate estimate of the cost of manufacture.

It makes practically no difference what kind of wood is used for the manufacture of alcohol, as all yield the same amount of alcohol per ton of wood. Oak, however, on account of the excessive amount of tannic acid which it contains, and which is a foe to fermentation, has to go through an additional treatment for the elimination of this acid before it can be fermented and its sugars converted into alcohol,

In a general way the process in this plant is as follows :—

The sawdust, which is drawn from a radius of about seventy-five miles from the plant, is put into a digester, and a predetermined amount of water and sulphurous acid is added. The digester is closed and sealed, and external heat applied until the pressure inside reaches about 100 pounds, at which pressure the contents are kept for a certain length of time, during which the cellulose in the wood is converted into dextrin and other sugars. The heat is then cut off and the usual sulphurous acid, which has been put into the digester simply to get the pressure to the required point, is reclaimed. The material in the digester, which has shrunk about 25 per cent, is then passed over to the separator, in which the acetic acid formed during the conversion is vaporised by means of a steam jet, and then collected. The converted sawdust is then brought over to the mash tanks, where its acidity is neutralised, and it is made into a mash which is fermented and distilled in the same way that an ordinary grain mash is handled in a whisky distillery.

The tailings from the still are first compressed to extract the water, and the final amount of moisture is taken out in a dryer heated by waste gases from the boilers. In France and England these dry tailings are made into stock food or brickettes ; or by the addition of a small amount of magnesia, are compressed into an artificial fireproof stone, which has a crushing strength of 18,000 pounds per square inch and a tensile strength of 6000 pounds.

Other experiments are being carried on at present for further results from these tailings, and while not at liberty to make public what these experiments are, I venture to predict that there is a good deal more in the tailings than has so far been got out of them.

The results obtained from the wood shipped from America were as follows :—

For every 3200 pounds of green refuse, which contains about 30 per cent moisture and is the equivalent of one long ton of theoretically dry wood, we obtained 21½ gallons of 188° proof alcohol, which is the equivalent of 38·6 gallons of proof alcohol. By experiment in the laboratory, we found that this yield should have been about 10 per cent higher, which loss was probably due to our inexperience in handling the apparatus.

In addition thereto will be obtained 76 pounds of acetic acid and ¾ of a ton of refuse, the latter being manufactured into stock food by the English and the French people.

The French chemist of the concern claims that under proper manipulation of the apparatus, and when everything is in working order, they obtain from their wood—and we should from ours—30 gallons of alcohol per ton of sawdust.

It is estimated that for every ton of theoretically dry wood, or, in other words, for every 3200 pounds of green sawdust, one should obtain :—

	Dollars.
30 galls. of 188° alcohol at 40 cents per gall...	12·00
76 pounds of acetic acid at 6 cents per pound..	4·56
¾ ton of stock food at 23·00 dollars per ton ..	17·25
	33·81
Less estimated cost of production	7·00
Net profit	26·81

If one takes into consideration that 1000 feet board measure of green lumber is the equivalent of 1¼ long tons of theoretically dry wood, this would make the net return of 33·51 dolls. per 1000 feet board measure.

This to the sceptic may sound like a wild dream, but the facts given in this article are based on actual results. Some people who have had occasion to look into this matter further have determined to go ahead and erect plants for the manufacture of alcohol, acetic acid, and stock food from wood waste, and I am at present designing a plant to be erected in Hadlock, Washington, having a capacity of 50 tons of sawdust per day, and another to be erected in Ontario, Canada, with a capacity of 100 tons of sawdust per day. These plants I hope to have in successful operation by the first of the year, and the day will not be far distant when it will pay the sawmill owners to go more deeply into the question of economy of waste material in the woods, as well as waste of power in the plant.

If it is figured that so-called wood waste returns only 10·00 dolls. per ton instead of 26·81, and, further, that it takes at least two tons of wood waste to equal one ton of coal in the production of steam, the sawmill owner will have to admit that the time to economise has arrived.—*Manufacturers' Record.*

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,*

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, &c.

By PERCY H. WALKER.

Introduction.

The Contracts Laboratory of the Bureau of Chemistry is called upon to examine a great variety of articles purchased by the Government. The character of the examinations made varies to such an extent that it is not possible to outline any general methods which are not subject to more or less variation according to the purpose for which the material is intended.

In this *Bulletin* are assembled methods which have been found useful in a large number of cases. As a general rule these methods, while not original, have been compiled from a variety of sources and modifications introduced when necessary. No attempt has been made, therefore, except in a few cases, to refer to the original source. Acknowledgments, however, are due to the following authorities :—Lunge, Lewkowitsch, Rideal, Fernbach, Hall, Perry, Hurst, Low, and many others. Nor has any attempt been made to give all of the methods for the examination of any of the materials mentioned, but only those which have been found most useful in this laboratory.

The methods are presented in this form because of their inaccessibility at present—scattered as they are throughout chemical literature—and because those selected from the mass of material on the subject have been tested in practice and found to be especially satisfactory.

Specific Gravity Determinations.

1. *Temperature Corrections.* It is almost the universal custom among oil chemists in this country to express the specific gravity of oils at 15·5° C. (60° F.) as compared with water at the same temperature. Since this temperature is generally far below that of the laboratory, the determination is frequently made at a higher temperature, and the specific gravity calculated, using the formula $G = G' + K(T - 15{\cdot}5^\circ\ C.)$, in which G = specific gravity at 15·5° C. ; G' = specific gravity at T, and K = mean correction for 1° C.

The correction K varies somewhat for different oils, but the value K = 0·00064 may be taken as sufficiently accurate in most cases for both hydrocarbon and fatty oils. (For the value of K for different fatty oils see "Allen's Commercial Organic Analysis," third edition, ii., Part I., 33, and for lubicating oils see Archbutt and Deeley, "Lubrication and Lubricants," p. 183). These corrections, however, only apply to specific gravities referred to water at 15·5° C. (60° F.). The common custom of determining specific gravity at higher temperatures compared with water at the same temperature as the oil gives values to which this correction does not apply. If the correction is applied to such values, the results obtained for 15·5° C. will contain large errors. This is well illustrated by the following example :—

* *Bulletin* No. 109, Revised, U.S. Department of Agriculture, Bureau of Chemistry.

The specific gravity of a sample of oil was carefully determined at two temperatures, with the following results :

1. Specific gravity at $\frac{15{\cdot}5^\circ\ \text{C.}}{15{\cdot}5^\circ\ \text{C.}} = 0{\cdot}9342.$

2. Specific gravity at $\frac{25^\circ\ \text{C.}}{25^\circ\ \text{C.}} = 0{\cdot}9298.$

If the temperature correction is applied to the second value, the result is as follows :—$0{\cdot}9298 + 9{\cdot}5 \times 0{\cdot}00064$ $0{\cdot}93588$ (specific gravity at 15·5° C.), an error far too large to be admissible. Now, from the known density of water

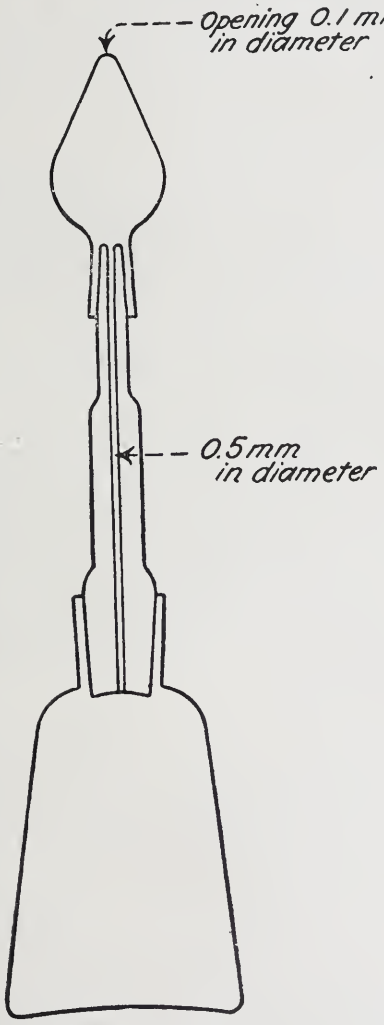


FIG. 1.—PYKNOMETER FOR VERY FLUID LIQUIDS. (Actual size).

at varying temperatures (Landholt, Bornstein, and Meyerhofer, "Physikalische Chemische Tabellen," p. 37 ; Bureau of Standards, *Circular* No. 19, p. 27) the specific gravity at $\frac{25^\circ\ \text{C.}}{15{\cdot}5^\circ\ \text{C.}}$ may be calculated from Equation 2, as follows :—

$$0{\cdot}9298 \times \frac{0{\cdot}997071}{0{\cdot}999050} = 0{\cdot}92795.$$

If to this value the correction is applied the result is $0{\cdot}92795 + 9{\cdot}5 \times 0{\cdot}00064 = 0{\cdot}93403$, a value differing less than two in the fourth place from that actually determined, which is sufficiently accurate for most commercial work.

It is a simple matter to determine the specific gravity at any selected temperature as compared with water at 15·5° C., but to do so most easily it is necessary to properly calibrate the pyknometer or plummet. The coefficient of cubical expansion of glass varies somewhat, and, while this correction should be applied when necessary in calibrating, care should always be taken to apply the correction for only a very few degrees. The Bureau of Standards in calibrating volumetric apparatus assumes the cubicle coefficient of expansion of glass per degree centigrade as equal to 0·000025, and if this value is always used, on determinations within a very few degrees of the desired temperature, no appreciable error will be made. Since it is not safe to assume that the cubical coefficient of expansion of glass is the same for all temperatures, apparatus should be calibrated at a temperature very near that at which the determination is to be made.

2. *Westphal Balance.*—The Westphal balance, on account of its convenience, is frequently used in making specific-gravity determinations, but it is difficult to determine the errors for this instrument. The weights can be easily tested, but the divisions on the arm are not easily tested, and both may be somewhat incorrect. It is better

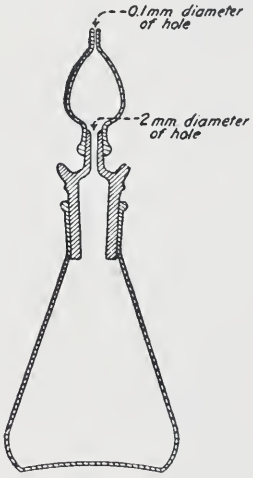


FIG. 2.—PYKNOMETER FOR VISCOUS LIQUIDS. (One-half actual size).

not to use a Westphal balance, but a plummet may be used on an analytical balance, which, when properly calibrated, is a very useful piece of apparatus, though the temperature is rather hard to control.

3. *Vacuum Weighing.*—It is not necessary to reduce weighings to vacuum, since the corrections entering in both numerator and denominator would not make any appreciable difference in the result. It should be understood that both in calibrating the apparatus and in making the specific gravity determinations all weights are made in air.

4. *Choice of Pyknometers.* For the most accurate work with very fluid oils the Sprengel tube is the most accurate form. This apparatus is difficult to clean, and for ordinary work a specific-gravity bottle, with a cap to take up expansion, is the most convenient. A thermometer as part of the apparatus adds to the cost and has little or no advantage ; in fact, it has some distinct disadvantages. Aside from errors in the thermometer, the liquid, if placed in the pyknometer at a low temperature and then allowed to stand at room temperature until the thermometer registers 15·5° C., may not be of the same temperature throughout. If a pyknometer without a thermometer is used, it is necessary to bring it to its final temperature by keeping it in a bath for some time. By filling the pyknometer at about 14° C., inserting the stopper, and

then placing it in a bath which is kept at 15·5° C. until no more liquid rises out of the capillary tube, one may be sure that the whole of the liquid in the pyknometer is at 15·5° C.

The form of pyknometer shown in Fig. 1 is excellent for very fluid oils, but it is not suitable for those that are very viscous. For the latter use the form shown in Fig. 2.

5. *Calibration of Pyknometers.*—Clean and dry the pyknometer, and weigh carefully after it has stood in the balance case for about thirty minutes. Fill with freshly boiled distilled water at about 14° C., insert the stopper, and place in a bath kept at exactly 15·5° C. When the temperature of the water in the pyknometer has risen to 15·5° C., which will be shown by the water ceasing to rise out of the capillary tube of the stopper, wipe off the water on the top of the stopper, place the cap on the stopper, remove from the bath, wipe dry, and let stand until it has come to room temperature, then weigh. This will give the water value of the pyknometer at 15·5° C. Calibrate the same pyknometer at 50° C., proceeding in the same way, except that the water used in filling the apparatus is about 47° C. and is brought up to 50° C. in a bath kept at exactly that temperature. Multiply the weight of water at 50° C. by $\frac{0{\cdot}99905}{0{\cdot}98807} = 1{\cdot}011125$. This product is the water value of the pyknometer at 50° C. In determining the specific gravity of any oil proceed as in calibrating, only substitute the oil for the freshly boiled water, and divide the weight of oil by the water value of the pyknometer. Results are expressed in specific gravity at $\frac{15{\cdot}5^\circ\text{ C.}}{15{\cdot}5^\circ\text{ C.}}$ or $\frac{50^\circ\text{ C.}}{15{\cdot}5^\circ\text{ C.}}$. If it is desired to calibrate the instrument at any other temperature, proceed in a similar manner and multiply the weight of water found by the density of water at 15·5° C. (0·99905) and divide by the density at the temperature used. (Use the tables of Landholt, Bornstein, and Meyerhofer, previously mentioned).

A plummet may be calibrated in a similar manner by calculating the water equivalent at 15·5° C. of the volume displaced at the different temperatures.

6. *Hydrometers.*—Hydrometers are frequently used by oil chemists, and when properly made are very good instruments. They should be calibrated at 15·5° C. (60° F.) and used at that temperature when exact results are desired. If a hydrometer is used at any other temperature (T), the results should be recorded at $\frac{T}{15{\cdot}5^\circ\text{ C.}}$ and also reduced to $\frac{15{\cdot}5^\circ\text{ C.}}{15{\cdot}5^\circ\text{ C.}}$ by applying the formula: $G = G' + K(T - 15{\cdot}5^\circ\text{ C.})$. Unless the determination is made at the temperature at which the hydrometer is calibrated the result should not be relied on beyond the third place. If more exact results are desired, do not use a hydrometer.

7. *Arbitrary Scales.*—The expression of specific gravity in terms of arbitrary scales, such as Baumé, is very objectionable, since there are a number of Baumé tables in print which differ widely. It is sometimes necessary, however, to report specific gravity in degrees Baumé. When this is the case determine the specific gravity in the usual manner, reduce, if necessary, to $\frac{15{\cdot}5^\circ\text{ C.}}{15{\cdot}5^\circ\text{ C.}}$, and find the degrees Baumé by reference to an American standard table. Such a table has been recalculated and published by the Bureau of Standards, *Circular* 19, and is calculated by means of the following formulæ:—

For liquids lighter than water—

$$B^\circ = \frac{140}{\text{Specific gravity at } 15{\cdot}5^\circ\text{ C.}} - 130.$$

For liquids heavier than water—

$$B^\circ = 145 - \frac{145}{\text{Specific gravity at } 15{\cdot}5^\circ\text{ C.}}$$

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 16th, 1910.

Prof. HAROLD B. DIXON, M.A., Ph.D., F.R.S., President, in the Chair.

(Concluded from p. 35).

185. "*New Synthesis of Thioxanthone and its Derivatives.*" By ERIC GORDON DAVIS and SAMUEL SMILES.

It was shown that thioxanthone may be synthesised by warming *o*-carboxybenzenesulphinic acid and benzene with concentrated sulphuric acid; the yields furnished by this process, however, are inferior to those obtained when *o*-thiolbenzoic acid is warmed with benzene and the same condensing agent, about 80 to 90 per cent of the required amount being then obtained.

Numerous derivatives have been prepared by the latter method, and the *methyl-*, *hydroxy-*, and *methoxythioxanthones* were described in detail, also the preparation of *naphthathioxanthone*, *aminonaphthathioxanthone*, and *naphthabisthioxanthone* has been accomplished by this method. The mechanism of the reaction was discussed, and the conclusion was drawn that the sulphoxylic acid, $(1)CO_2H{\cdot}C_6H_4{\cdot}SOH(2)$ is formed as an intermediate product.

186. "*The Intramolecular Re-arrangements of Diphenylmethane Orthosulphoxide.*" By THOMAS PERCY HILDITCH and SAMUEL SMILES.

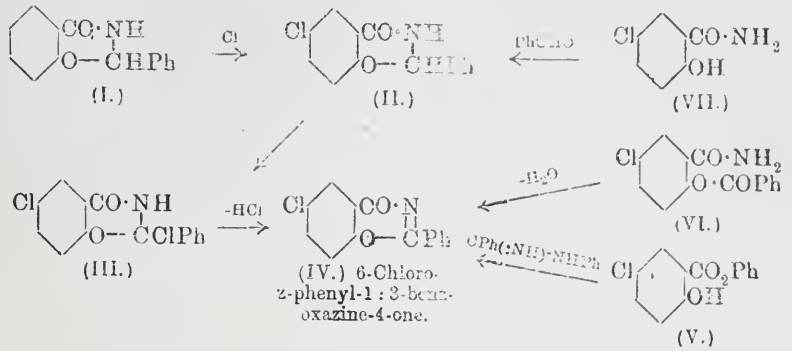
The *o*-sulphoxide of diphenylmethane is obtained by the interaction of hydrogen dioxide and thioxanthen. It is oxidised by potassium permanganate to diphenylmethane *o*-sulphone, and thus differs from thioxanthydrol, which yields thioxanthone on oxidation under similar conditions. This sulphoxide is transformed by fusion, or by being warmed above its melting-point in certain solvents, into thioxanthydrol, and by acid reagents it is converted into the salts of dibenzocarbothionium. Werner's statement (*Ber.*, 1901, xxxiv., 3311) that thioxanthydrol is converted by acids into the salts of that base has been confirmed, although here the change appears to be more rapid than with the sulphoxide. The study of these intramolecular changes is being continued.

187. "*6-Chloro-2-phenyl-1 : 3-benzoxazine-4-one and Related Derivatives.*" By ARTHUR WALSH TITHERLEY and ERNEST CHISLETT HUGHES.

The chlorination of 2-phenyldihydro-1 : 3-benzoxazine-4-one (phenylbenzometoxazone) (I.) leads first to the production of the 6-chloro-derivative (m. p. 214°) (II.), in which, by further action, the hydrogen atom (2) in the oxazine ring is displaced. The resulting dichloro-derivative (III.), however, cannot exist, and by loss of hydrogen chloride yields the chloro-derivative (m. p. 215°) (IV.) of the unsaturated cyclic compound recently isolated by Titherley (*Trans.*, 1910, xcvii., 200). The unsaturated chloro-derivative (IV.) has also been synthesised from phenyl 5-chlorosalicylate (V.) and phenylbenzamidine, and from 5-chloro-O-benzoylsalicylamide (VI.) by internal condensation with hydrogen chloride, whilst the simple chloro-derivative (II.) has been synthesised by the condensation of 5-chlorosalicylamide (VII.) and benzaldehyde (see next page).

The chloro-derivative (II.) with pyridine and alkali yields the open-chain isomeride, *syn*-benzylidine-5-chlorosalicylamide, $OH{\cdot}C_6H_3Cl{\cdot}CO{\cdot}N{:}CHPh$, which is very labile, and on heating rapidly reverts to the cyclic form (II.).

O-Benzoyl 5-chlorosalicylamide (VI.), which may be readily obtained by the pyridine benzoylation method at −15°, rearranges, on heating, to N-benzoyl 5-chlorosalicylamide, $OH{\cdot}C_6H_3Cl{\cdot}CO{\cdot}NH{\cdot}COPh$, and reversible rearrangement of the latter occurs in boiling acetic acid,



The same N-benzoyl derivative is produced by the hydrolytic rupture of the oxazine ring in (IV.) under the influence of acids.

188. "*Separation of the Metals of the Tin Group.*" By Robert Martin Caven.

The following modification of Walker's method (*Trans.* 1903, lxxxiii., 184) for the qualitative separation of the metals of the tin group has been found rapid and satisfactory. The mixed sulphides are re-precipitated from their solution in alkali, collected, washed, and boiled with concentrated hydrochloric acid according to a well-known method of separation, and the remaining arsenious sulphide, filtered off from the diluted solution, may then be identified in the usual manner by making use of its solubility in ammonium carbonate solution.

To the filtrate, free from hydrogen sulphide and containing antimonious and stannic chlorides, potassium hydroxide is added until the hydroxides precipitated are just re-dissolved in excess of alkali. Bromine water is then added until the solution remains yellow; thus antimonite, which would be hydrolysed in presence of ammonium chloride, is oxidised to antimonate.

The addition of solid ammonium chloride first causes the evolution of nitrogen, because of the hypobromite present; then stannic hydroxide separates, and, after boiling, is collected.

The filtrate contains only the antimony, which is precipitated as antimonic sulphide on acidifying and passing hydrogen sulphide.

The advantage of this scheme of analysis is that it employs Walker's excellent method of separating tin from antimony without postponing the identification of arsenic, which may result in small quantities of this element, present finally as arsenate, being missed by students.

189. "*The Formation and Reactions of Imino-compounds.* Part XIII. *The Constitution of Ethyl β-Imino-α-cyanoglutarate and of its Alkyl Derivatives.*" By Arthur Fred Campbell and Jocelyn Field Thorpe.

Ethyl β-imino-α-cyanoglutarate,—

$$CO_2Et\cdot CH_2\cdot C(NH_2):C(CN)\cdot CO_2Et,$$

reacts entirely as an amino-compound, and appears to have no imino-phase. It is therefore a substituted ethyl glutaconate, and it is now found that in many of its reactions this amino-derivative behaves like glutaconic acid. Thus when one methyl group is introduced, ethyl β-imino-α′-cyano-α-methylglutarate,—

$$CO_2Et\cdot CHMe\cdot C(NH_2):C(CN)\cdot CO_2Et,$$

is formed as sole product, whereas when two methyl groups are introduced, the second methyl combines with both the α-carbon atom and the α′-carbon atom, forming ethyl β-imino-α′-cyano-αα-dimethylglutarate,—

$$CO_2Et\cdot CMe_2\cdot C(NH_2):C(CN)\cdot CO_2Et,$$

and ethyl β-imino-α′-cyano-αα′-dimethylglutarate, $CO_2Et\cdot CMe:C(NH_2)\cdot CMe(CN)\cdot CO_2Et$, showing therefore that there is tautomerism between the α- and α′-carbon atoms as there is between the α- and γ-carbon atoms of glutaconic acid.

It has also been found that ethyl β-imino-α′-cyano-αα-dimethylglutarate can be isolated in two stereoisomeric forms, showing that the substitution of the two α-carbon atoms in ethyl β-imino-α-cyano-glutarate and the consequent "fixing" of the double bond leads, as in the derivatives of glutaconic acid, to the isolation of stereoisomeric modifications.

The production of pyrrole derivatives from the sodium compound of ethyl β-imino-α′-cyano-α-methylglutarate by the action of iodoacetonitrile was also described, the formation of these substances proving that the mobile hydrogen atom acted preferentially on the α′-carbon atom.

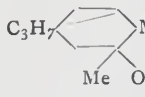
190. "p-*Hydroxyazo-derivatives of Quinoline.*" By John Jacob Fox.

Hydroxyazo-derivatives of quinoline, such as 5-p-*aminobenzeneazo-8-hydroxyquinoline*, were described, having the hydroxyl group in the ortho-position with respect to the nitrogen in the quinoline nucleus; and the properties of these substances were compared with the corresponding derivatives in which the hydroxyl group was not in the quinoline nucleus. It was shown that whilst the latter could be acetylated and ethylated in the usual way, the former did not under ordinary conditions yield acetyl or alkyloxy-derivatives. It was pointed out that the carbonium structure for the polyhydrochlorides was inadequate to account for the marked instability of the hydrochlorides of the hydroxyazo-derivatives of 8-hydroxyquinoline as compared with quinolineazophenol.

The absorption spectra show bands of which the heads occur at oscillation frequencies in about the same position as in the simpler hydroxyazo-derivatives, as, for example, dimethylaminobenzeneazophenol.

191. "*A Contribution to the Study of Tanacetone (β-Thujone) and some of its Derivatives.*" By David Thomson.

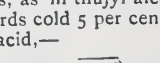
Tanacetone (β-thujone), when treated with magnesium methyl iodide, yields two tertiary homothujyl alcohols,—



:

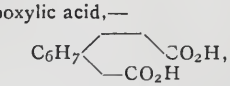
one a solid, melting at 84°, and having $[\alpha]_D$ −30·5°; the other a liquid, boiling at 204°, and having $[\alpha]_D$ +35°. In both these alcohols, as in thujyl alcohol, the *cyclo*propane ring is stable towards cold 5 per cent sulphuric acid.

α-Thujaketonic acid,—



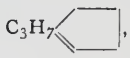
is decomposed by boiling with 20 per cent hydrochloric acid solution, with the formation of an unsaturated hydrocarbon, which in odour and boiling-point is similar to dihydro-Ψ-cumene.

α-Thujadicarboxylic acid,—

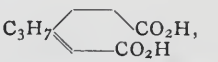


prepared from α-thujaketonic acid by oxidation, is quite stable towards boiling 20 per cent hydrochloric acid or boiling 10 per cent sodium hydroxide. α-Thujadicarboxylic acid can be easily esterified in the ordinary way. The *dimethyl*, *diethyl*, *di*-n-*propyl*, *diisobutyl*, and *diisoamyl* esters have been prepared. All are colourless, odourless liquids.

The dimethyl and diethyl esters of α-thujadicarboxylic acid give a sodio-derivative, the decomposition products of which are tanacetophorone,—



β-thujadicarboxylic acid,—



and an unknown inactive dicarboxylic acid, $C_9H_{14}O_4$, melting at 150—151°.

192. "*Pentane-* and iso*Pentane-αβδ-tricarboxylic Acids.*" By EDWARD HOPE and WILLIAM HENRY PERKIN, jun.

These acids were prepared for the purpose of comparison with acids which had been obtained by the degradation of some new terpenes which will shortly be described. *Ethyl β-cyanopentane-αβδ-tricarboxylate*, $CO_2Et{\cdot}CH_2{\cdot}C(CN)(CO_2Et){\cdot}CH_2{\cdot}CHMe{\cdot}CO_2Et$, prepared by the action of ethyl bromoacetate on the sodium derivative of ethyl γ - cyano - α - methylglutarate, $CO_2Et{\cdot}CH(CN){\cdot}CH_2{\cdot}CHMe{\cdot}CO_2Et$, distils at about 195—215°/17 mm., and, when digested with dilute sulphuric acid and the resulting crude acid esterified, is converted into *ethyl pentane-αβδ-tricarboxylate*. This ester distils at 178—182°/19 mm., and yields on hydrolysis *pentane-αβδ-tricarboxylic acid*, $CO_2H{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H$, which melts at about 158°.

Ethyl β - cyanoisopentane - αβδ - tricarboxylate,— $CO_2Et{\cdot}CH_2{\cdot}C(CN)(CO_2Et){\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Et$, prepared in a similar manner from ethyl γ-cyano-β-methylglutarate, $CO_2Et{\cdot}CH(CN){\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Et$, and ethyl bromoacetate, distils at about 195—215°/13 mm., and yields, on hydrolysis and subsequent esterification, *ethyl* iso*pentane-αβδ-tricarboxylate*, which distils at 180—183°/20 mm.

iso*Pentane-αβδ-tricarboxylic acid*,—

$$CO_2H{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H,$$

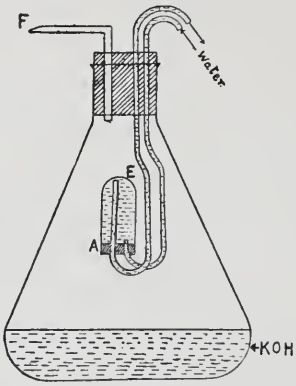
melts at about 154—156°.

193. "*The Action of Pure Air and Water on Iron and Steel.*" (Preliminary Note). By JOHN ALBERT NEWTON FRIEND.

The electrolytic theory of the corrosion of iron first advanced by Whitney in 1903 has, during the past few years, been received with increasing favour, chiefly because a considerable number of investigators, both in this country and in America, have failed to retain iron in a rust-free condition in the presence of liquid water and oxygen. The absence of rust in Moody's experiments is attributed to passivity induced by the chromic acid employed, as also to the presence of alkali dissolved out of the glass vessels containing the iron. The results of the author's own experiments (*Journ. Iron and Steel Inst.*, 1908, No. II., 5) are explained away in a somewhat similar manner (see W. H. Walker, *Ibid.*, 1909, No. I., 69; and Friend, *Ibid.*, 1909, No. II., 257).

In order to demonstrate the untenability of such an explanation, the following experiment has been devised, which shows in a remarkably clear and simple manner that pure water and air alone are incapable of effecting the corrosion of pure iron and steel.

AE is a hollow cylinder (of iron or steel) closed at one end. The open end is fitted to a tightly fitting rubber stopper bearing two glass tubes, as shown in the figure, and arranged in such a way that cold water can circulate freely through them. The cylinder is well polished with sand-paper, and secured as shown inside a conical flask containing about 150 cc. of 3N-potassium hydroxide solution. The air is partly removed, and the vessel hermetically sealed at F. The flask is now placed to half its depth in a water-bath at 100°, after having been thoroughly shaken to remove every trace of carbon dioxide from its walls, &c., and a current of cold water passed through AE. The pressure of the air is not sufficiently reduced to allow the potash to boil, nevertheless pure water vapour condenses on AE and drips off, thus slowly washing it free from alkali.



After this process has been continued for several days, not a trace of alkali remains on AE, as is readily shown by opening the apparatus and testing with phenolphthalein. Nevertheless, if the iron is pure, it remains quite bright, thus proving that pure water and pure air combined are without action on pure iron. In one of the experiments two spots of rust were formed after twenty-four hours at the bend E, although the rest of the metal remained bright for several days when the apparatus was opened. This rusting was undoubtedly due to traces of slag in the metal, for on repeating the experiment, after thoroughly cleaning the iron, two spots of rust formed again in a precisely similar place. Repetition with a fresh sample of steel gave no rust whatever.

(We are indebted to the Chemical Society for permission to reproduce this illustration).

194. "iso*Quinoline Derivatives.* Part V. *The Constitution of the Reduction Products of Papaverine*" (continued). By FRANK LEE PYMAN and WILLIAM COLEBROOK REYNOLDS.

In Part II. of this series (*Trans.*, 1909, xcv., 1610) one of the authors showed that Goldschmiedt's "tetrahydropapaverine" was in reality a dihydropapaverine, and termed it "1 : 2-dihydropapaverine." In view, however, of the properties of its N-methyl derivative, the constitution of the base is regarded as unsettled. It is proposed to designate it *pavine*. N-*Methyl-pavine* is formed together with laudanosine by the reduction of papaverine methyl salts, and may also be obtained by the methylation of pavine; it is also formed in the oxidation of laudanosine.

The further investigation of this compound is in progress.

195. "*The Specific Rotatory Power of Hyoscyamine and the Relation between that of Alkaloids and their Salts.*" By FRANCIS HOWARD CARR and WILLIAM COLEBROOK REYNOLDS.

The specific rotatory power of pure-*l*-hyoscyamine is −22·0° in 50 per cent ethyl alcohol, whilst that of its basic ion taken in aqueous solutions of the salt is −32·5°.

Barrowcliff and Tutin (*Trans.*, 1909, xcv., 1966) stated that the lower value for the free base was due to racemisation occurring in the process of preparing it from its salts.

It is now shown that racemisation does not take place so very readily as supposed by these authors—pure *d*- and *l*-hyoscyamine having $[\alpha]_D - 22{\cdot}0°$—but that the specific rotatory power of hyoscyamine and of many other alkaloids differs widely from that of their respective basic ions taken in solution of a salt.

The free alkaloids behave as though they are not ionised, or only partly so, when dissolved in water or in 50 per cent ethyl alcohol, the nitrogen retaining a triad function.

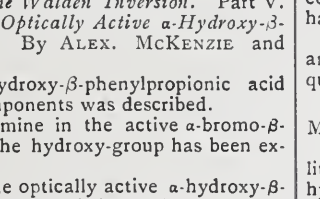
The rotatory power of a number of alkaloids and their salts has been determined, and some observations bearing upon the influence of different solvents have been made.

196. "*Experiments on the Walden Inversion.* Part V. *The Interconversion of the Optically Active α-Hydroxy-β-phenyl Propionic Acids.*" By Alex. McKenzie and Henry Wren.

The resolution of *r*-α-hydroxy-β-phenylpropionic acid into its optically active components was described.

The displacement of bromine in the active α-bromo-β-phenylpropionic acids by the hydroxy-group has been examined.

The interconversion of the optically active α-hydroxy-β-phenylpropionic acids has been carried out, thus—



This is the first example recorded where phosphorus pentachloride appears to act abnormally. The isomeric acids, $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H$, $C_6H_5{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$, and $\begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}OH\\CO_2H\end{matrix}$, thus differ from one another from the point of view of the Walden inversion.

197. "*Carthamine.*" By Tokuhei Kametaka and Arthur George Perkin.

It was suggested (*Proc.*, 1909, xxv., 223) that carthamine, the colouring matter of safflower, possessed the formula $C_{15}H_{14}O_7$, rather than $C_{14}H_{16}O_7$, originally assigned to it by Schlieper (*Annalen*, 1846, lviii., 362), but further experiment now indicates that the much higher formula $C_{25}H_{24}O_{12}$ is most probably correct. Carthamine, when dried in the air, crystallises with $2H_2O$, gives with dilute alcoholic potassium acetate the salt $C_{25}H_{23}O_{12}K$, green, iridescent needles, and an amorphous benzoyl compound, probably $C_{25}H_{17}O_{12}(C_7H_5O)_7$, melting at 230—232°, has been obtained. Although Schlieper obtained a yellow substance, $C_{14}H_{14}O_9$, by boiling carthamine with alcohol, and Radcliffe (*Journ. Soc. Dyers*, 1897, xiii., 159) noticed a similar decomposition, experiment has failed to reproduce this. When carthamine is boiled with alcoholic aniline it gives a substance $C_{25}H_{24}O_{12},C_6H_7N$, long yellow needles, melting and decomposing at 276—278°, soluble in alkalis with a yellow colour, and for which the name *aniline xanthocarthaminate* is proposed.

β-Naphthylamine gives the compound $C_{25}H_{24}O_{12},C_{10}H_9N$, orange leaflets, melting and decomposing at 266—268°, and the corresponding derivative of ψ-cumidine forms orange leaflets, melting and decomposing at 290°. A molecular weight determination of carthamine kindly carried out by Dr. Barger by his microscopic method gave M.W. = 551, whereas the formula $C_{25}H_{24}O_{12}$ requires M.W. = 516.

With nitric acid carthamine gives picric acid. When digested with boiling 50 per cent potassium hydroxide, it yields *p*-coumaric acid and *p*-hydroxybenzaldehyde, and by the prolonged action of 1 per cent alkali or strong baryta water is similarly decomposed. Hydrogen peroxide in presence of sodium carbonate also produces *p*-coumaric acid, and in a similar way the crude methylation product of carthamine yields with hydrogen peroxide, *p*-methoxycinnamic acid, and probably *p*-methoxycinnamaldehyde, and with chromic acid, anisaldehyde and anisic acid.

198. "*Note on Gynocardin and Gynocardase.*" By Charles Watson Moore and Frank Tutin.

Gynocardinic acid (*Trans.*, 1905, lxxxvii., 349), when methylated by means of dry silver oxide and methyl iodide, yields *methyl pentamethylgynocardinate*, $C_{12}H_{14}O_4(OMe)_5{\cdot}CO_2Me$, which is a liquid boiling at 220°/15 mm. No definite products could be obtained by the hydrolysis of this methyl derivative.

Gynocardin possesses feebly acidic properties, and yields compounds with the alkali metals; the *sodium* derivative has the formula $C_{13}H_{18}O_9NNa$.

The action of emulsin and of gynocardase on gynocardin, amygdalin, *l*-mandelonitrile glucoside, and salicin has been quantitatively determined.

199. "*Note on Quercitrin.*" By Charles Watson Moore.

The glucoside quercitrin is usually stated in chemical literature to possess the formula $C_{21}H_{22}O_{12}$, and its hydrolysis, with the formation of quercetin and rhamnose, has therefore been represented as follows:—
$C_{21}H_{22}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{14}O_6$.

It is evident, however, that this equation cannot be correct, inasmuch as it is now known that rhamnose possesses the formula $C_6H_{12}O_5$, but that it crystallises with one molecule of water. According to Brauns (*Arch. Pharm.*, 1904, ccxlii., 561), quercitrin possesses the formula $C_{21}H_{20}O_{11},2H_2O$, and its hydrolysis would therefore take place quite normally by the absorption of one molecule of water as follows: $C_{21}H_{20}O_{11} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_5$.

In the course of some experiments on quercitrin it was deemed desirable to confirm the formula assigned to it by Brauns (*loc. cit.*), and in this connection some other observations concerning the glucoside may be recorded:—

1·6548 of air-dried glucoside, when heated at 125°, lost 0·1274 H_2O. $H_2O = 7{\cdot}7$.

0·1794 (anhydrous substance) gave 0·3700 CO_2 and 0·0734 H_2O. $C = 56{\cdot}2$; $H = 4{\cdot}5$.

$C_{21}H_{20}O_{11},2H_2O$ requires $H_2O = 7{\cdot}4$ per cent.
$C_{21}H_{20}O_{11}$ requires $C = 56{\cdot}2$; $H = 4{\cdot}5$ per cent.

These results are thus seen to be in agreement with the formula assigned to quercitrin by Brauns (*loc. cit.*).

The melting-points of carefully purified quercitrin have likewise been observed to differ considerably from those recorded in the literature. It has, for example, been stated (compare Brauns, *loc. cit.*) that the air-dried glucoside melts at 174—176°, and the anhydrous substance at 168°. The correct melting-points are, however, 183—185° and 250—252° respectively.

A determination of the specific rotatory power of the air-dried glucoside gave the following result:—

0·2224, made up to 20 cc. with pyridine, gave $[\alpha]_D - 1°34'$ in a 1-dcm. tube, whence $[\alpha]_D - 140{\cdot}9°$.

If to an alcoholic solution of quercitrin an excess of sodium ethoxide be added, a *trisodium* derivative is precipitated. This forms a dark yellow powder, sparingly soluble in cold alcohol:—

0·2974 gave 0·0870 Na_2CO_3. $Na = 12{\cdot}9$.
$C_{21}H_{17}O_{11}Na_3$ requires $Na = 13{\cdot}4$ per cent.

Attempts to prepare the corresponding methyl derivative from the sodium derivative were unsuccessful, as were also those to obtain a crystalline acetyl or benzoyl derivative of quercitrin.

Colloidal Nature of Chromopolysulphuric Acids.—Pablo Martinez Strong.—The examination of aqueous solutions of chromopolysulphuric acid under the ultramicroscope shows that these acids have a colloidal nature, the characteristic Brownian movements being easily detected.—*Comptes Rendus*, cl., No. 19.

NOTICES OF BOOKS.

Allen's Commercial Organic Analysis. Volume II., Fourth Edition. Edited by Henry Leffmann, M.A., M.D., and W. A. Davis, B.Sc , A.C.G.I. London: J. and A. Churchill. 1910.

So many changes have necessarily been made in the text of the fourth edition of "Allen's Commercial Organic Analysis" that it is practically a new work; the little which has been left of the old text has been subjected to a very careful revision by the staff of distinguished collaborators who are responsible for the new edition. Volume II. deals with the fixed oils, butter-fat, lard, linseed oil, &c., saponification products, and higher fatty acids. The general properties of each group of substances are described, and details are given of general and special methods of analysis. The detection of foreign matter in the products is treated very fully, and the results of a great number of typical analyses are included.

Compulsory Working and Revocation of Patents. By Ernest Lunge. London: Stevens and Sons, Ltd. 1910.

In this book the author discusses the compulsory working of patents both in the past and in the present, and also gives a code of the law and practice concerning the Patents and Designs Acts, 1907, Section 27. Some moot points are discussed in the memoranda which are appended to the code. The author makes his opinion of the effects of every system of compulsory working very clear, and has some original observations to make on the probable consequences of the Act, and the defects both in its principle and in its details.

Merck's Chemicals. April, 1910. Darmstadt: E. Merck.

This catalogue consists of about 200 pages of lists of fine chemicals and reagents for bacteriological, microscopical, pharmaceutical, &c., purposes, as well as drugs and minerals. Prices for both large and small quantities are usually quoted, and, although the firm makes it a rule to deal with wholesale dealers only, arrangements can be made to despatch consignments direct to purchasers, thus effecting much saving of time.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xliii., No. 8, 1910.

Alkaline Saponification of Glycerin Trinitrate.—E. Berl and Max Delpy.—The action of alkalis on glycerin trinitrate gives the following products:—Nitrate, nitrite, alkali-cyanide, ammonia, glycerin trinitrate, $\alpha\alpha$-glycerin dinitrate, mesoxalic acid, oxalic acid, carbon dioxide, as well as volatile acids and aldehydes which have not been identified. According to the experimental conditions more or less of the nitric acid is decomposed into lower oxidation products—nitrous acid, hydroxylamine, and ammonia, while primary and secondary oxidation products of glycerin, mesoxalic acid, oxalic acid, and carbon dioxide are simultaneously formed. The formation of glycerin dinitrate shows that a normal gradual saponification occurs, and that it is not until a complete saponification has taken place that the organic components are oxidised and the nitric acid is reduced. Since some unchanged trinitrate and the dinitrate are always among the products of the complete saponification of glycerin trinitrate, obviously alkaline saponification is not the surest way of destroying the explosive.

Quantitative Colorimetric Determination of Traces of Hydrocyanic Acid.—E. Berl and Max Delpy.—The solution is made alkaline with caustic potash, ferrous sulphate solution is added (at least 2 mols. $FeSO_4$ to 1 mol. HCN), the mixture is allowed to stand for ten minutes, boiled, allowed to cool, and made acid with hydrochloric acid. The colour of the liquid is then compared with that of a comparison solution containing a known amount of hydrocyanic acid, and thus the HCN present is determined.

Preparation of Pure Argon and Nitrogen.—Franz Fischer and Otto Hähnel.—The authors have devised a new apparatus by which perfectly pure argon can be prepared; the same apparatus can also be used in the preparation of other gases in the pure state. The density of perfectly pure argon is 19·945. This value practically agrees with that stated by Ramsey. The density of nitrogen when prepared pure in the same apparatus is 14·018. As purification proceeded a brilliant luminescence was noticed when argon was passed through the apparatus. Similar phenomena have been obtained in the case of neon and helium, while with nitrogen they do not appear.

New Researches on Argon's Power of Forming Compounds.—Franz Fischer and Fritz Schröter.—To produce an arc in liquid argon Fischer and Iliovici's apparatus was employed and found quite satisfactory, and by means of it the action of forty-five metals on argon was investigated. Some of the metals were pulverised, forming a black powder, while others were unaffected. With the exception of Groups I. and VII. of the Periodic Table the elements which are not pulverised are in the left hand vertical rows of the columns, and those which are pulverised are on the right hand side of the columns. The elements in the two top horizontal rows must be regarded as being on the left hand side of their columns.

Modifications of Metals Produced by Electric Pulverisation in Liquid Argon.—Franz Fischer and Fritz Schröter.—In arc discharges between metallic electrodes in pure liquid argon no argon compounds are formed, nor could it be shown even that such exist at the temperature of liquid air. Argon compounds, if they exist, must be much more explosive than cadmium nitride, otherwise they would be formed in the same way as the latter. A number of metals were obtained in a new form by pulverisation. Lithium and sodium were obtained as brown powders, potassium, rubidium, and cæsium as relatively stable blue powders. Zinc and cadmium gave black powders, which, however, were stable only at the temperature of liquid air. It was found that the finely divided pulverisation products usually possess no adsorption power for argon at room temperature. But this is not the case with the black form of zinc at the temperature of liquid air. Some metals were obtained in the pyrophoric state, *e.g.*, the alkalis, zinc, tin, indium, and manganese.

New Metal - Nitrogen Compounds.—Franz Fischer and Fritz Schröter.—By sudden cooling in a liquid mixture of argon and nitrogen the unstable nitrides of all the metals of the right hand vertical rows of the columns of the Periodic Table can be prepared directly from their elements as well as Hg, Tl, Pb, and Bi nitrides. In liquid mixtures of 90 per cent argon and 10 per cent nitrogen the nitrides of Na, K, Rb, Zn, Cd, Hg, In, Tl, Sn, Pb, As, Sb, Bi, Te, and Mn are formed. These compounds are true nitrides and not azides; they were never obtained pure, but always contained excess of metal in the form of dust. The nitrides of higher atomic weight are explosive, *e.g.*, Cd, Hg, Pb, and Bi nitrides. The others decompose on gently warming, but only with a slight explosion or else quite quietly. No nitrides of Zn, Cd, Pb, Bi, and Ni were obtained in gaseous nitrogen; traces of nitrides of Sb and Sn were formed, and large quantities of manganese nitride. With the exception of the first group of the Periodic System the left hand sides of the vertical columns contain elements whose nitrides are stable at room temperature, while the elements on the right hand side form nitrides which are unstable at room temperature and are decomposed by a blow or on warming. Possibly the nitrogen of the earth's atmosphere was once combined in the form of endothermic nitrides.

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NOTE ON CARBON MONOSULPHIDE.

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and
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No chemical double decomposition is known which results in the direct production of a substance of the composition of carbon monosulphide. We have discovered such a reaction.

Thiophosgene reacts rapidly with nickel carbonyl at the ordinary temperature, and less rapidly at —20° C., to produce a brown solid and a large volume of carbon monoxide. (The thiophosgene used was obtained from Schuchardt, and when purified by distillation boiled at 72—73° C. under 730 mm. pressure). Although the reaction is apparently violent the mixture rather falls in temperature just as the similar mixture of nickel carbonyl and oxalyl chloride does (*Chem. Soc. Trans.*, 1909, xcv., p. 1909). The solid was found to consist of nickel chloride, which was readily extracted by water, and a brown solid containing carbon and sulphur. The reaction takes place readily between the two liquids or their vapours alone, or between the liquids mixed with dry ether, petroleum ether, carbon tetrachloride, or chloroform, and even when the two substances had been carefully dried by contact with pure phosphorus pentoxide.

It seemed possible that the reaction had taken place according to the equation —

$$x\mathrm{Ni(CO)_4} + x\mathrm{CSCl_2} = x\mathrm{NiCl_2} + 4x\mathrm{CO} + (\mathrm{CS})_x$$

to produce a solid polymeric form of carbon monosulphide.

Quantitative experiments gave results in agreement with this view, as may be seen from the following examples.

0·860 grm. $CSCl_2$ and 1·5 grms. $Ni(CO)_4$ in dry ether gave 1·21 grms. of solid, of which 0·89 grm. was $NiCl_2$ and 0·40 grm. solid insoluble in water and dried at 100° C. According to the equation there should have been 1·30 grms. of the mixed solids, of which 0·97 grm. should have been $NiCl_2$ and 0·33 grm. $(CS)_x$.

4·7 grms. $CSCl_2$ and excess $Ni(CO)_4$, 9 grms., gave 7 grms. solid, of which 5·1 grms. were $NiCl_2$ and 2 grms. solid insoluble in water and dried at 100° C.

The equation given above requires 5·3 grms. $NiCl_2$ and 1·8 grms. $(CS)_x$.

As will be seen later, the solid retains water very persistently, so that the weight obtained would probably be in excess of that expected.

The percentages of carbon and sulphur were determined in the mixed solids after washing with ether and drying at 100° C., with the following results : —

0·5070 grm. gave 0·1090 grm. CO_2 and 0·0320 grm. H_2O ; hence C = 5·87 per cent.

0·4230 grm. gave 0·4895 grm. $BaSO_4$; hence S = 15·9 per cent.

Atomic ratio—C : S = 0·489 : 0·497.

This rendered it extremely probable that the equation given above represents the course of the reaction.

In attempting to purify the carbon monosulphide some difficulties were encountered. Unfortunately, no convenient reagent other than water has been found for separating the nickel chloride from the other product, and this admittedly introduces difficulties, since water is retained by the solid, and it has not yet been found possible to obtain the substance quite free from water. Even after heating to 150° C. or 200° C. under reduced pressure for over an hour, as much as 10 per cent of water was found on combustion. Then, in spite of the fact that excess of nickel carbonyl was always used, traces of thiophosgene were found to be retained persistently by the solid.

The following process was adopted for the preparation of specimens for analysis. Thiophosgene was allowed to react with slightly more than one molecular proportion of nickel carbonyl mixed with about ten times its volume of dry ether, carbon tetrachloride, or chloroform at the ordinary temperature, the usual precautions being taken to exclude moisture. After standing for some hours the solid product was separated by filtration, washed with the solvent, extracted with the solvent for about half-an-hour in a Soxhlet apparatus, and then heated to 100° C. This product was now extracted with water in the same manner until all the nickel chloride had been removed. It was found that the solid still contained small quantities of nickel in a form insoluble in water ; it was therefore extracted repeatedly with dilute hydrochloric acid until nickel could no longer be detected in the acid solution, and it was then washed with water until free from chloride. The product was finally dried by heating, first to 100° and then to 150° C., and sometimes to 200° C. under reduced pressure. In some cases the odour of thiophosgene could be detected in the vapour given off on heating under reduced pressure ; the difficulty of removing this substance is, of course, much increased owing to the ease with which it polymerises. In all cases the product was proved to be free from chlorine before being used.

It was found that at the higher temperature, 200° C. or more, sulphuretted hydrogen was produced in small quantity, probably from the interaction of water with the carbon monosulphide.

The carbon in the product was estimated by combustion in a tube containing lead chromate, and the sulphur was estimated by Carius's method. The variable quantity of water found on combustion is assumed to be present in water, either free or possibly combined, and is taken as impurity in calculating the percentages of carbon and sulphur.

The following analyses are selected as typical of those which have been made :—

1. *Solvent, ether. Product dried at* 150° C.

0·4220 grm. gave 0·3901 grm. CO_2 and 0·0416 grm. H_2O ; hence C = 25·2 per cent, or, corrected for water present, 27·9 per cent.

0·1588 grm. gave 0·7432 grm. $BaSO_4$; hence S = 64·3 per cent, or, corrected for the amount of water present, 71·3 per cent.

2. *Solvent, chloroform. Substance dried at* 150° C.

0·2190 grm. gave 0·2010 grm. CO_2 and 0·0150 grm. H_2O ; hence C found = 25·1 per cent, or, corrected for the amount of water present, C = 26·9 per cent.

0·3175 grm. gave 1·5210 grms. $BaSO_4$; hence S found = 65·8 per cent, or, corrected for the amount of water present, S = 72·2 per cent.

Analyses of the products obtained when no solvent was used, or when carbon tetrachloride was used, gave similar results. Also washing with carbon disulphide did not alter the composition of the substance. The product obtained when petroleum ether was used as solvent usually gave a higher percentage of carbon. Thus, for example, a specimen dried at 160° C. gave the following result :—

0·3248 grm. gave 0·3205 grm. CO_2 and 0·0285 grm. H_2O ; hence C found = 26·5 per cent, or, corrected for the water present, C = 29·6 per cent.

This may be due to the production of complicated carbon compounds from the petroleum ether, and some evidence of their presence was obtained during the process of drying under reduced pressure.

CS requires C 27·3 and S 72·7 per cent.

It may therefore be fairly concluded that the reaction between thiophosgene and nickel carbonyl takes place

according to the equation given above, and yields a polymeric form of carbon monosulphide.

It is curious that the product should polymerise so readily, seeing that the reaction takes place at the ordinary temperature, and it is well known that polymeric forms of carbon monoxide have not been obtained.

On different occasions Baudrimont, Thomsen, and Deninger each believed that he had isolated a gaseous carbon monosulphide. Modern theory enables us to predict, from a comparison of the critical temperatures of the two oxides of carbon and carbon disulphide, that the boiling-point of the hypothetical carbon monosulphide would be about —130° C. Those claims were subsequently shown to have been founded on error.

A polymeric form of carbon monosulphide appears to have been obtained by Sidot (*Comptes Rendus*, 1872, lxxiv., 179; 1875, lxxxi., 32), who stated that pure carbon disulphide decomposed, on exposure to sunlight for some months, into sulphur, and a substance stated to be carbon monosulphide, which is described as a maroon red powder, odourless, tasteless, only slightly soluble in hot carbon disulphide and ether, insoluble in other solvents, and having a specific gravity of 1·66. The substance is dissolved by hot concentrated nitric acid to a red solution, is ignited by the monohydrate of nitric acid, but is not attacked by hydrochloric or sulphuric acids. It is dissolved by concentrated caustic potash to a deep brown solution, from which acids precipitate the substance unchanged. At 200° C. this carbon monosulphide is stated to decompose into carbon and sulphur, but if heated with sulphur, carbon disulphide and a white crystalline solid are produced. The only quantitative datum which is referred to is a determination of the proportion of sulphur to the solid, and no analyses are given.

The properties of carbon monosulphide as prepared by us agree in some respects with Sidot's description, but there are also important differences in other respects.

Carbon monosulphide is a brown powder, which in some cases closely resembles some forms of carbon in appearance.

Determinations of the specific gravity of the finely divided powder gave a mean value of about 1·6; after compression into a solid block it gave the value 1·83. In this condition the substance is a non-conductor of electricity. The molecular volume is therefore 24, which is about 10 per cent greater than the sum of the atomic volumes of its constituents.

A general comparison of the molecular volumes of the oxides and sulphides, as far as we know them, can now be made and is interesting:—

The molecular volume of solid carbon monoxide is 28.
The molecular volume of solid carbon dioxide is 28·7 at −78° C., or 27 at −185° C.
The molecular volume of solid carbon disulphide is 52·4 at −188° C.

Thus it appears that the volumes of carbon monoxide and dioxide are the same, whereas carbon monosulphide has a volume which is approximately only half as great as that of carbon disulphide, and it is therefore clear that the carbon monosulphide described is formed from carbon disulphide with considerable contraction, and this is confirmatory that it is a condensed molecule.

Carbon monosulphide is practically insoluble in alcohol, ether, benzene, and petroleum ether; it is slightly soluble in carbon disulphide, ethylene dibromide, nitrobenzene, naphthalene, and phenol to give deeply coloured, reddish brown solutions. Unfortunately, the solubility is too small to allow of determinations of the molecular weight of the compound.

The behaviour of carbon monosulphide with sulphuric acid is characteristic and interesting. It is not affected by the dilute acid; but with the concentrated acid in the cold or at higher temperatures it forms a brownish purple solution, the colour of which is only slowly destroyed at the boiling-point of the acid, when carbon dioxide and sulphur dioxide are evolved. On pouring the solution in concentrated sulphuric acid into water a flocculent precipitate separates, which after washing and drying was found, on analysis, to be unchanged carbon monosulphide.

The compound is dissolved by concentrated nitric acid acid at the ordinary temperature to a reddish solution, the colour of which is only destroyed on long heating; for this reason, although some sulphuric acid seems to be produced at once, the whole of the sulphur is not converted into sulphuric acid until the solution has been heated for a long time, and low percentages of sulphur were obtained by Carius's method, unless the heating had been continued at about 150° C. for some hours. On one occasion only did the compound ignite on coming into contact with nitric acid.

Carbon monosulphide dissolves in an aqueous or alcoholic solution of ammonia, ammonium sulphide, caustic potash, potassium sulphide, or potassium hydrosulphide to give a deep brown solution, from which acids precipitate the carbon monosulphide apparently unchanged.

On heating the solid in a high vacuum no change took place below 360° C., except the evolution of a small quantity of sulphuretted hydrogen, and when mercury was present no mercury sulphide was formed. At a low red-heat a liquid was given off which was found to be carbon disulphide. Even after heating the compound to a red-heat in a quartz tube, in which a high vacuum was maintained by means of charcoal cooled in liquid air, for an hour and a-half, the residue still contained some sulphur, though it was chiefly carbon. Some quantitative experiments were made, of which the following is typical:—0·380 grm., after heating to a red-heat for an hour and a-half, left 0·1075 grm. residue which contained 15 per cent of sulphur.

It is therefore probable that on heating the carbon monosulphide is decomposed according to the following equation:—$2(CS)_x = xC + xCS_2$, but that the change is very slow.

On heating carbon monosulphide in a current of dry hydrogen, sulphuretted hydrogen was produced, and the residue which was left was almost free from sulphur. On heating in a current of dry chlorine the substance melted and evolved sulphur chloride, together with a little thiophosgene, and a residue of carbon was left.

The most important differences between carbon monosulphide as prepared by us and the substance described by Sidot as resulting from the long action of light, are the colour, the action of sulphuric acid, and the decomposition by heat. Also, we were not able to get carbon disulphide by heating the compound with sulphur to the boiling-point of sulphur.

The examination of the properties of carbon monosulphide is being continued.—*Proceedings of the Royal Society*, A, lxxxiii., p. 408.

Determination of Tartaric Acid.—C. Beys.—Tartaric acid can be accurately determined in raw materials by the following method. The substance (1—2 grms.) is heated for thirty minutes on the water-bath with its own weight of diluted (1 : 20) sulphuric acid. After cooling 5 volumes of alcohol are added little by little and 10 volumes of ether. The mixture is filtered and washed with the same volume of ether and alcohol. The filtered liquid is neutralised (using phenolphthalein) with an alcoholic solution of caustic potash. Then an excess of the same solution is added. The temperature of the liquid is raised to 38°, and after cooling the liquid A is decanted from the precipitate B. To A glacial acetic acid is added, the tartaric acid in it is precipitated as potassium bitartrate, which is filtered and washed. B is dissolved in boiling water, and glacial acetic acid is added to the solution. The tartaric acid is precipitated as potassium bitartrate and alcohol is added. The mixture is well shaken, filtered after an hour, washed with alcohol, and then dissolved with the precipitate from A in boiling water. The solution is finally titrated by Goldenberg and Géromont's method.—*Comptes Rendus*, cl., No. 20.

NOTE ON THE KJELDAHL ESTIMATION OF NITROGEN IN FATTY SUBSTANCES.

By J. A. BROWN, F.I.C.

On distilling off the ammonia into standard acid in the Kjeldahl estimation of nitrogen in such substances as cheese, milk, &c., the author has frequently found that a troublesome frothing ensues in the alkaline liquor, which compels the operation to be conducted very slowly, and with constant attention, to prevent the alkaline liquor frothing over into the distillate and vitiating the result. Believing that other analysts may experience the same trouble, the following simple device for overcoming the difficulty may prove generally useful.

The author has found that the frothing is caused by traces of fatty acids, which escape decomposition in the digestion with strong H_2SO_4 by volatilising and condensing firmly, in minute discs, on the long neck of the Kjeldahl flask, where they are with great difficulty, if at all, rinsed back into the bulb. (These fatty acids appear to be identical with those which constitute the insoluble volatile fatty acids in the Reichert distillation of butters, *i.e.*, the Polenske value). The undecomposed fatty acids combine with the excess of alkali, added for the subsequent distillation of ammonia, to form a soap, which causes the liquid to froth when boiled.

This may be prevented by diluting the digested substance, previous to adding excess of alkali, to about 100 cc. with distilled water and boiling briskly until only about 40 cc. remains in the flask. On now making alkaline and proceeding in the usual way, the distillation can be conducted with the greatest rapidity, without even attending to the initial ebullition.

These experiments were carried out in the laboratory of Mr. R. A. Cripps, F.I.C., to whom my thanks are due.

ON A NEW VOLUMETRIC METHOD FOR COBALT AND NICKEL.

By GEORGE S. JAMIESON.

The well-known application of potassium ferrocyanide to the volumetric determination of lead and zinc has led the writer to investigate the application of this method to the determination of cobalt and nickel, and conditions have been found under which concordant and accurate results may be obtained. As far as can be found by consulting the literature, this method has not been previously suggested.

It is believed that the most important practical application of the method will be in the determination of nickel in steel, for it can be carried out in the presence of iron, it is rapid, and requires no expensive reagents. As far as ease and rapidity are concerned, it appears that the cyanide method as applied in the presence of iron by C. M. Johnson (*Journ. Am. Chem. Soc.*, 1907, xxix., 1201), and also by Campbell and Arthur (*Ibid.*, 1908, xxx., 1116), is the only one which can compete with it. The writer has found that by combining the modifications of the authors just referred to, the cyanide method may be decidedly improved, as will be shown by the description and the results which are given beyond. This choice between the ferrocyanide and the cyanide methods for nickel in steel would depend upon the preference of the operator, but it is to be observed that the cyanide method is not applicable to large amounts of cobalt on account of a peculiar dark precipitate produced under these circumstances during the cyanide titration which interferes with the end reaction.

For the ferrocyanide titration a solution containing 20 grms. per litre of potassium ferrocyanide is recommended as a suitable strength for most work. Then each cc. will be equivalent to about 3 mgrms. of cobalt or nickel. To standardise this it is best to employ a cobalt or nickel solution of known strength prepared either from pure salts in known volume or by gravimetric standardisation. Three equal portions of this solution containing about 0·1 grm. of the metal are taken in beakers. Ten cc. of a 10 per cent solution of ferric chloride and 2 to 3 grms. of citric acid are added to each, and then ammonia is added with stirring until the solution has a faint odour of the reagent. It is important that the excess of ammonia should not be too great, as in this case the results will be irregular. The solutions are then diluted to about 100 cc. with hot water, and are brought to a temperature of 65—75°. The ferrocyanide solution is now run in slowly with constant stirring. After a few drops of the ferrocyanide have been added, the nickel or cobalt ferrocyanide begins to precipitate. As the titration progresses, a drop or two of the solution is removed by means of the stirring rod to a paraffined white plate and acidified with a drop of dilute acetic acid. The solution is thoroughly stirred, and a second test is made in the same way beside the other. This pair of tests is designated as No. 1, and a record is made of the volume of ferrocyanide used at this point. The titration is carried on in this way until a greenish colour is developed in about five minutes at a definite point in the series. The most convenient practice is to titrate the first portion roughly, and then to get the exact point with the other two portions. The important precautions are to avoid more than a slight excess of ammonia and to titrate slowly with thorough stirring.

The actual determinations are made in exactly the same way as the standardisation just described. The method cannot be applied in the presence of such metals as copper, zinc, and manganese which react with potassium ferrocyanide. In the case of substances containing a considerable amount of iron, which must be in the ferric condition, no addition of ferric chloride is required.

The results are given in Table I. obtained with varying quantities of cobalt and nickel solutions.

Table I.—*One cc.* $K_4Fe(CN)_6$ *Solution* = 0·002105 *grm.* Co, *or* 0·001885 Ni.

No.	Co taken. Grm.	$K_4Fe(CN)_6$ used (cc.).	Co found. Grm.	Error.
1	0·0632	30·1	0·0633	+0·0001
2	0·0379	18·0	0·0379	—
3	0·0379	18·0	0·0379	—
4	0·0063	3·1	0·0065	+0·0002
5	0·0442	21·0	0·0442	—
6	0·0505	24·0	0·0505	—
7	0·0537	25·7	0·0541	+0·0004
8	0·0287	13·5	0·0284	−0·0003
9	0·0144	4·6 (*a*)	0·0145	+0·0001
10	0·0144	4·6 (*a*)	0·0145	+0·0001
	Ni taken.		Ni found.	
11	0·0462	24·5	0·0462	—
12	0·0770	40·8	0·0769	−0·0001
13	0·0770	40·8	0·0769	−0·0001
14	0·0377	19·8	0·0373	−0·0004

(*a*) Another ferrocyanide solution.

The following directions may be followed for the determination of nickel in steel :—Weigh out 1·000 grm. of borings into a 150 cc. flask, add 10 to 15 cc. of dilute nitric acid (equal volumes of 1·42 sp. gr. acid and water). Cover the flask with an inverted crucible cover, and when the violent action is over, remove cover, and boil gently over a free flame, keeping the flask in constant motion and inclined at about 45°, until the steel is decomposed. (If a steel is encountered which is not entirely dissolved by nitric acid, add a drop or two of strong hydrochloric acid or a crystal of potassium chlorate, and continue the boiling). Add 10 cc. of concentrated nitric acid as soon as the steel is in solution, heat to boiling again, and add half a grm. of solid potassium chlorate. Boil until the chlorine is expelled. Add the same quantity of chlorate again, and boil for about two minutes. Then allow the flask to cool a little, and filter off the manganese dioxide on a Gooch crucible

washing with as small a quantity as possible of cold water. Proceed then according to the method already described. It is to be observed that the presence of a large amount of iron, as in the case of nickel steel, somewhat retards the appearance of the end reaction. It is advisable to standardise the ferrocyanide solution in the presence of about the same amount of iron as is present in 1 grm. of steel. The determinations given in Table II. were made in the three samples of steel by the method just described. The nickel in A was checked by the electrolytic, ether-cyanide, and dimethyl-glyoxime methods. The analyses of samples B and C were completed before the results by other methods were known.

TABLE II.

No.	Ni steel. Grms.	$K_4Fe(CN)_6$. Cc.	Nickel. Per cent.	Ni by other methods.
1A	1·0000	11·55	3·63	3·65
2A	1·0000	11·50	3·62	3·65
3A	1·0000	11·60	3·64	3·65
1B	1·0000	11·00	3·46	3·47
2B	1·0000	10·90	3·43	3·47
3B	1·0000	11·10	3·49	3·47
4B	1·0000	11·10	3·49	3·47
1C	1·0000	11·20	3·52	3·50
2C	1·0000	11·10	3·49	3·50
3C	1·0000	11·20	3·52	3·50

Duplicate analyses of nickel in a steel can be made in this way in about an hour, and the results show that the method is accurate.

The following application of the cyanide method to the determination of nickel in steel was worked out by the writer before the papers of Johnson and Campbell and Arthur, which have been previously referred to, had been seen. The former investigator used a large amount of citric acid, while the latter used a large amount of sodium pyrophosphate. The writer uses both of these reagents together, but in much smaller quantity. The directions, according to the writer's modification, are as follows :—

Take 0·5 grm. of borings in a 150 cc. flask, add 10 cc. of 1 : 1 nitric acid, and dissolve according to the directions given for the ferrocyanide method. If the metal contains more than 0·5 per cent of manganese, the writer prefers to remove it according to the directions just referred to. Add to the nitric acid solution 2 to 3 grms. of citric acid and 2 grms. of anhydrous sodium pyrophosphate, then add ammonia slowly with stirring until the precipitate formed at first just dissolves and the solution acquires a very faint odour of ammonia. If too much ammonia has been used, it must be nearly neutralised by the careful addition of nitric acid. Dilute to about 150 cc., and cool to a temperature below 20°, add a few drops of a 10 per cent solution of potassium iodide, and enough tenth-normal silver nitrate solution, the volume of which must be noted, to produce a distinct turbidity. Then run in potassium cyanide solution very slowly with stirring until the turbidity just disappears, and the solution lightens to a golden-yellow colour. The solution should remain bright for five minutes, otherwise the titration is incomplete. Sometimes it happens that the turbidity disappears when only one-third to one-half of the required amount of cyanide has been used, but in this case upon the addition of a drop or two of silver nitrate, or upon waiting a moment, the turbidity reappears. The end-point is best observed when the beaker is placed upon a white paper having an elliptical hole in it under which is placed a black glazed paper for contrast. In making the calculation the proper deduction for the silver nitrate used should be made.

The potassium cyanide solution should be standardised by means of the tenth-normal silver nitrate. To do this take 20 cc. in a beaker, dilute to about 150 cc. with cold water, add ammonia until the odour is distinct but slight, add a few drops of 10 per cent potassium iodide solution, run in silver nitrate until a distinct turbidity is produced, and then finish by slowly adding the cyanide solution until the turbidity just disappears. The theoretical amount of nickel per 1 cc. of tenth-normal solution is 0·002935 grm., but instead of using this value it is perhaps preferable to standardise the solution with a steel of known content in nickel. The theoretical value was used in the test analyses given in Table III., which indicate very satisfactory results for the method.

TABLE III.

No.	Ni steel. Grm.	KCN. Cc.	Nickel. Per cent.	Ni by other methods.
1A	0·5000	6·70	3·70	3·65
2A	0·5000	6·62	3·67	3·65
3A	0·5000	6·60	3·66	3·65
1B	0·5000	6·25	3·46	3·47
2B	0·5000	6·26	3·48	3·47

—*Journal of the American Chemical Society*, xxxii., No. 6.

DETERMINATION OF SULPHUR IN BRASS AND BRONZE.

By GUSTAV THURNAUER.

FOR the determination of sulphur in brass and bronze the method heretofore used has been rather circuitous by oxidising the borings, filings, or sawings with aqua regia, or with a solution of chlorine or bromine, repeated evaporation with HCl to remove the nitric acid or the other oxidising agents, digesting with sodium carbonate, filtering from the rather voluminous precipitate, and determining the sulphur in the filtrate by precipitation with barium chloride in the ordinary manner after proper acidulation.

The writer has attempted to adapt the method used for years for the determination of sulphur in organic compounds to the making of sulphur determinations in brasses and bronzes, and has been able to obtain thoroughly satisfactory results in the following manner.

With the aid of a mill-cut file, fine enough to make filings which will easily pass through a 100-mesh sieve, filings of the metal are prepared (file across machined face of test-bar) and passed through a sieve. Any small particles of iron from the file are removed with the aid of a magnet.

One grm. of these filings is thoroughly mixed with 6 grms. of a powder consisting of 2 parts of potassium chlorate and 1 part of sodium carbonate.

In a wrought iron crucible there is first placed a small quantity of sodium carbonate to cover the bottom, then the mixture of the filings with the carbonate and chlorate is carefully transferred into this crucible, and finally the whole mixture is again covered over with a small quantity of sodium carbonate and chlorate. The crucible is then covered with a porcelain cover, and heated first slowly and then to a fairly high temperature over a Bunsen flame until the whole mass is thoroughly melted.

The fusion after cooling is digested with hot water The salts which contain all the sulphur as sulphate are filtered from the oxide residue, the filtrate is acidulated with hydrochloric acid and boiled to remove all carbonic acid. The solution is then neutralised with ammonia and made slightly acid by carefully adding hydrochloric acid until an acid reaction appears, and then 2 or 3 drops in excess are added. The solution is then brought to boiling, and a boiling solution of barium chloride is added.

Letting the solution stand for one-half hour in a warm place, but not boiling it further, all the sulphur will be precipitated as barium sulphate, which can then be readily filtered and washed.

The weight of the barium sulphate times 0·13734 is equivalent to the weight of sulphur in the sample.

Using an iron crucible does not appreciably increase the figures obtained, as the sulphur taken up from the iron amounts, at the outside, to $^1/_{100}$ to $^2/_{100}$ of 1 per cent.

If great accuracy, however, is required, a silver crucible can be used, or a nickel crucible.

It is self understood, of course, that all the reagents must be tested for a possible presence of sulphur before they are used in this method.—*Journal of Industrial and Engineering Chemistry*, ii., No. 6.

THE DETERMINATION OF ZINC BY WEIGHING AS SULPHATE.

By EUGENE C. SULLIVAN and W. C. TAYLOR.

This method is similar to the determination of cadmium, manganese, cobalt, magnesium, and calcium as sulphate. It has been in use by one of the writers for some years, and has given perfectly satisfactory results. The zinc is precipitated customarily as sulphide from a hot solution slightly acid with sulphuric or hydrochloric acid, to which ammonia is added during precipitation until the solution is but faintly acid. Precipitation made in this way is complete, and the precipitate is readily filtered and requires washing with hot water only (see Waring, "On Precipitation from Formic Acid Solution," *Journ. Am. Chem. Soc.*, 1904, xxvi., 27). As will be shown presently, removal of all traces of ammonium salts is not necessary. The zinc sulphide is washed into a deep beaker with as little water as possible, and dissolved in hydrochloric acid which has trickled through the filter-paper in order to take up any sulphide still adhering. To avoid effervescence during subsequent evaporation the solution in the covered beaker is boiled until hydrogen sulphide is completely expelled; it is then transferred to a weighed porcelain crucible and evaporated on the water-bath after addition of only a little more than the quantity of sulphuric acid necessary to form zinc sulphate. When no further evaporation takes place, the crucible is placed in a small air-bath, either a Hillebrand radiator (*Bull.* 305, *United States Geological Survey*, p. 29) or a large porcelain crucible fitted with asbestos ring as described by Treadwell ("Quantitative Analyses," fourth edition, p. 24). The excess of sulphuric acid having been removed by heating in such an air-bath, the crucible is cautiously subjected to the direct heat of the Bunsen flame, and finally heated to redness for several minutes. The crucible with zinc sulphate is coloured in the desiccator and weighed.

The results are as a rule accurate to within one or two-tenths of 1 per cent.

A solution of zinc chloride was made by dissolving J. T. Baker's chemically pure "analysed" zinc in hydrochloric acid and diluting so that 50 cc. of solution contained 0·3005 grm. zinc. In measured volumes of this solution the zinc was determined as sulphate, and, for comparison, as pyrophosphate by the method given by Waring (*Journ. Am. Chem. Soc.*, 1904, xxvi., 28).

In these determinations the solution for analysis was measured out by one of the writers, and the determination made by the other, so that the analyst had no knowledge of the result which he was expected to get.

Table I.—*Determination of Zinc as Sulphate and Pyrophosphate, with Calculated Results.*

Zinc found (grm.).	Zinc calculated (grm.).
As Sulphate.	
0·3043	0·3035
0·1541	0·1533
0·0909	0·0909
0·2428	0·2425
As Pyrophosphate.	
0·2861	0·2854
0·1656	0·1656
0·2224	0·2223

To determine whether or not the presence of small quantities of ammonium chloride affects the result, either by remaining unvolatilised as sulphate or by causing volatilisation of zinc chloride, zinc chloride solutions were evaporated with sulphuric acid and a few milligrms. of ammonium chloride. The outcome of these experiments (Table II.) makes it clear that for this determination it is not necessary to wash precipitated zinc sulphide perfectly free from ammonium chloride which may contaminate it. It should be added, however, that larger quantities of ammonium chloride (100 mgrms. and over) cause low results.

Table II.—*Influence of Ammonium Chloride on Determination of Zinc as Sulphate.*

Zinc found (grm.)	0·1803	0·1804
Zinc calculated (grm.)	0·1803	0·1804

—*Journal of Industrial and Engineering Chemistry*, i., No. 7.

AN AUTOMATIC TOEPLER PUMP, DESIGNED TO COLLECT THE GAS FROM THE APPARATUS BEING EXHAUSTED.*

By BERTRAM D. STEELE, D.Sc.

During the investigation of certain dissociating compounds containing sulphur dioxide, it became necessary to exhaust constantly certain apparatus for a prolonged period. After several days had been spent in manipulating a Toepler pump of the usual pattern, an automatic Toepler pump was designed and constructed.

The pump that was required was one which not only should be capable of being worked automatically for long periods, but also one by means of which it should be possible to deliver samples of the extracted gas when desired, and if necessary to collect the whole of such gas for examination.

These requirements are satisfactorily fulfilled by the pump which is described in the following paper. It will be best described in three sections, all of which are shown diagrammatically in the figure.

The pump proper is an ordinary Toepler pump, and is represented in the figure by the parts A and B and various adjuncts.

The collecting apparatus is represented by the parts C and D and connecting tubes.

The automatic controlling apparatus is represented by *s*, F, E, and *q*.

The pump proper consists of the stroke-cylinder A and the reservoir B, these being connected by the U-tube *d*. This U-tube, which is about 8 mm. in internal diameter, is provided at its lowest point with a short side-tube, by means of which the mercury can be removed from the pump if necessary, and it is constricted at one point to a diameter of about 2 mm. This constriction regulates the flow of mercury and renders it impossible to break the apparatus by a sudden blow of the mercury, even at the highest exhaustion. The U-tube in its shorter arm is 800 mm. long, in order that either A or B may be put into communication with the atmosphere whilst the other vessel is exhausted.

The stroke-cylinder A is provided, in the usual manner, with a ground-glass valve, *a*, and a manometer, *b*, and the apparatus to be exhausted is attached on the other side of the phosphoric-anhydride tube and the stopcock, *c*.

The reservoir B is connected with the water-pump by the tube *e*, and to prevent the possibility of water entering B, this tube is made 85 cm. long and is provided at its lower end with a mercury trap, *z*, of special design.

It has been found that very rapid currents of air can be sucked through this trap without a single globule of mercury being carried into the water-pump.

Two other tubes are attached to the reservoir B, one of

* A Paper read before the Physical Society.

which, *m*, is connected with the regulating apparatus E, and the other, *n*, with the mercury trap, *k*.

The collecting apparatus was designed to enable either the whole or a portion of the extracted gas to be withdrawn and collected.

In this apparatus the receiving bulb C is in direct communication with the stroke-cylinder A by means of the millimetre capillary tube, *f*, and with the atmosphere by means of a similar tube, *g*, which is attached to the top of the bulb. The U-tube *h* connects C with the subsidiary reservoir D, and from the slight enlargement at *i* a tube, *x*, is extended downwards and dips into the vessel F. The top of the bulb D is connected through the ground-glass valve and mercury trap *k* with the top of the reservoir B, and by the tube *l* with the middle of its under surface. The essential part of the automatic controlling apparatus consists of two portions. The bulb E with the test-tube *p*, joined together as shown by the 8-millimetre bore-tube *o*, and the branched tube *q*, which is of the shape shown in the figure, and is constricted to a fine capillary at the point *r*.

The longer arm of this tube reaches to the bottom of the vessel E, the shorter to the bottom of the tube *p*.

The vessels *s* and F are arranged so that any overflow of mercury from either of them finds its way into *p*.

The tube *q* is attached to *m* by rubber pressure tubing, which can be closed by the screw pinchcock at *u*, and each of the tubes, *l* and *x*, are cut and the parts joined by pressure tubing, which in the same manner can be closed by screw pinchcocks.

The volumes of the various vessels are approximately as follows :—

The stroke-cylinder	A	.. .. ..	300 cc.
The reservoir	B	.. .. ..	600 „
The collector	C	.. .. ..	100 „
The reservoir	D	.. .. ..	130 „
The bulb	E	.. .. ..	150 „

It is essential that the U-tube *d*, and the tubes *e*, *f*, and *g*, should be over 80 cm. in length.

The various levels of the various bulbs are as follows :—

The bottom of the reservoir B is placed 30 cm. below the top of the tube *f*, and 10 cm. below the connection between A and the valve *a*, at *v*. The bottom of the reservoir D is situated 16 cm. above the highest point of the tube *g*.

The shorter limb of the U-tube *h* is 25 cm. long, and the enlargement *i* is 75 cm. above the level of the side-delivery tube on F.

Twenty pounds of mercury are required to work a pump of the foregoing dimensions.

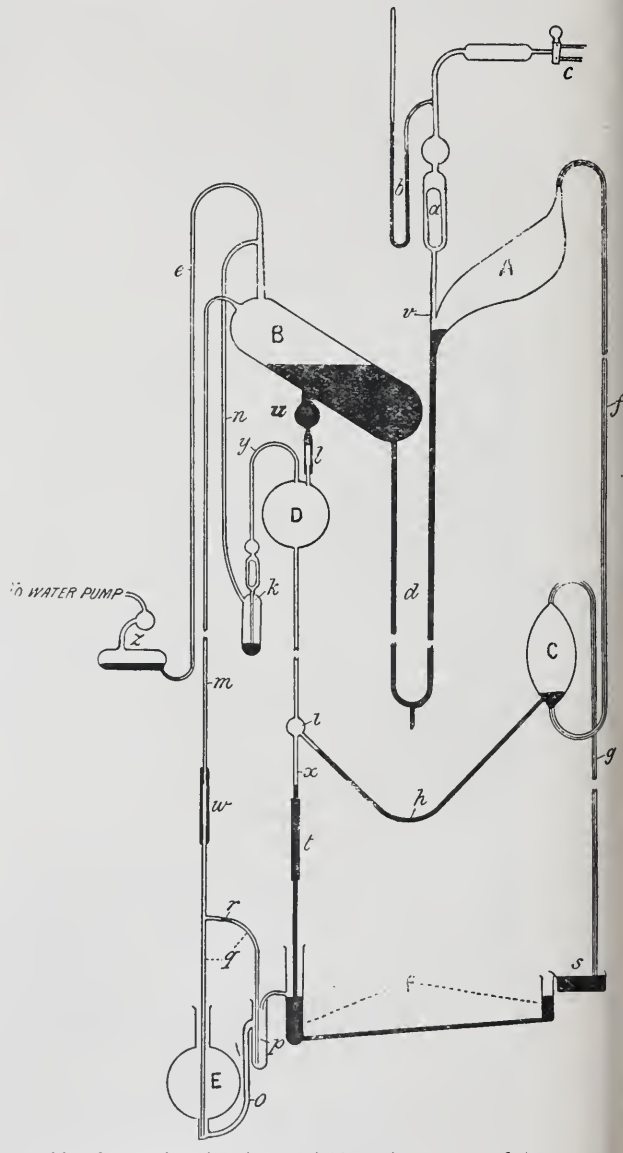
Filling the Pump.

Before starting to fill the pump, the stopcock *c* and the pinchcock on *l* are closed, and mercury is poured into the vessels *s* and F, and into the traps *z* and *k*. The trap *k* is is provided with a side-tube at the point *y*, to enable this to be done, and when sufficient mercury has been inserted this tube is sealed off. The water-pump is now connected at the trap *z*, and the mercury required to fill the pump is poured into E. Under the action of the water-pump, which must be sufficiently powerful to reduce the pressure in the apparatus to 10 or 15 cm. (whilst the side-tube is open to the atmosphere), the mercury rises in the tube *m*. Air is, however, slowly leaking in through the constricted branch of *q*, and this air breaks the mercury in *m* into columns which are carried over into B. In this way the whole of the mercury required is pumped rapidly from E into B.

Working the Pump.

It has been already stated that the pump was designed—(1) To discharge the extracted gas into the water-pump, (2) to collect samples of the gas for examination, and (3) to collect the whole of the gas from any piece of apparatus. The manner of working of the pump will be best shown by describing in detail the course of one complete stroke when it is working as required for Case I.

Starting from the time when a small quantity of the mercury required for filling the pump remains in E, and when the pressure in A, B, C, and D has been reduced to 10 or 15 cm., it will be seen that with the removal of the last globule of mercury from E into B, air can freely enter the latter vessel through the tube *m*. The water-pump is not



capable of removing the air as quickly as it enters, and the consequent rise in pressure causes the mercury to rise in A, and, driving the gas before it into the receiver *c*, it overflows through the tubes *h* and *t* into the vessel F, from this into *p*, and finally through *o* into the large bulb E. This overflowing mercury closes first the constricted and then the open end of the branched tube *q*, and thus cuts off the supply of air to the reservoir B.

The water-pump now reduces the pressure in the reservoirs B and D, and as a consequence the mercury immediately begins to flow back through the U-tube *d*, from A into B, and the overflow into F and *p* ceases.

About forty seconds after the closing of the tube *q* the mercury will have fallen to the point *v*, and in the meantime the mercury in *p* has been slowly syphoning through the branched tube *q* into the bulb E.

With the construction used, the time required to empty *p* is eighty seconds, and there is therefore an interval of forty seconds between the opening of the communication at *v* and the emptying of the tube *p*. During this time the apparatus to be exhausted remains in communication with the stroke-cylinder A. Following the last globule of mercury which syphons from *p* into E, air enters through the shorter branch *q*, and the mercury in E is pumped bach into the reservoir B, and finally, when all the mercury has been removed from E, air again enters freely through the tube *m*, and another stroke begins. The gas that accumulates in C finds its way through the tube *h*, the bulb D, and the trap *k*, to the water-pump.

Case 2.—If it is desired to collect samples of the gas, this can be done as follows :—

A test-tube of the size required is filled with mercury, and inverted over the turned-up end of the tube *g*, the pinchcock *t* is closed, and the following stroke of the pump mercury flows, by way of *f*, *c*, and *h*, into the bulb D. When a quantity more than sufficient to fill the bulb C has accumulated here, the pressure in D is caused to rise by opening the pinchcock on the tube *e*, when the gas in C is forced into the tube placed to receive it. The excess of mercury flowing into *s* finds its way as before in *p* and E.

Finally, the pinchcock *e* is closed, that at *t* opened, and the cycle proceeds as previously described.

Case 3.—Should it be desired to collect the whole of the gas from the apparatus being exhausted, the pinchcock *t* must be kept closed, and a vessel to receive the gas must be placed as before over the end of *g*. If the pressure in the apparatus is low, that is, if the quantity of gas to be collected is very small, the gas is displaced from C at every stroke of the pump, and the overflowing mercury finds its way from *s*, through F, into *p* and E.

If the pressure is more than 1 or 2 cm., it is necessary to manipulate the pinchcock on *l*.

In the great majority of instances it is only during the first five or six strokes of the pump that this will be necessary, and in this case it is most convenient to open *l* at the end of each stroke, exactly as described in case 2.

Should the vessel to be exhausted be very large, the pinchcock *l* must be regulated so that the mercury contained in the bulb *w* flows into D at such a rate that the last drop of mercury, followed by air, enters D at the moment when the latter has become about half full of mercury. If *l* is properly regulated, it is found that mercury flows through it only when the tube *m* is open to the atmosphere, and not when the reservoir B is exhausted by the water-pump.

In obtaining high exhaustion it is advisable to leave the stroke-cylinder A in open communication with the apparatus to be exhausted for a longer time than forty seconds. This object is obtained by attaching a side-tube to *p*, the capacity of which increases the volume of mercury which must syphon through *q* at every stroke.

The quantity of mercury, and hence the time of flow, can be regulated by sliding a well-fitting glass piston in this subsidiary tube.

The time occupied by a complete stroke of the pump that is described here is 160 seconds, during forty of which the communication at *v* is open. By the use of the subsidiary tube on *p* (not shown in the diagram) the total time is increased to four minutes, that during which *v* is open is increased in two minutes.

In order to stop the pump, all that is necessary is to close the pinchcock *u* when the tube *m* contains mercury, and then to disconnect the water-pump at *z* when the vessel A is empty of mercury. To start the pump afresh, the pump is attached to *z* and the pinchcock *u* is opened.

OPTICALLY ACTIVE NON-SUGAR OF THE SUGAR BEET.

By W. H. REES.

During the past two years considerable attention has been paid in European countries to the cause of excessive unaccountable loss of sugar in beet-sugar factories. The reason of this has been attributed to climatic conditions which have developed a new substance in the beet that is optically active and is either eliminated or destroyed in the processes of the factory. To the present time, however, no one has published an account of having definitely determined just how, or where, in the process, this loss occurs ; or of having obtained from the beet or factory products a dextro-rotatory substance which would be destroyed or eliminated by the factory processes. A summary by K. Andrlik, of the published articles concerning the existence of such a dextro-rotatary substance, was published in the *Zeit. Zuckerindustrie in Böhmen*, August, 1909. In the October and November numbers, 1909, Dr. O. E. Kopecky has fully described his experiments along this line, extending over a period of eight years, and has left little room for doubt that there has been present in the beets on which he worked a substance that indicated a higher per cent of sugar by the direct method of estimating sugar than by the inversion method. In the same journal, December, 1908, Ing. Fr. Herles described his experiments in which he found that the action of lime and heat on beet juice caused a reduction in the polarisation (this report is supplemented in Andrlik's article above referred to), and while Herles has been unable to satisfy many chemists as to the truth of his discovery, he has, in accordance with my experience, undoubtedly located the station where the greatest apparent loss of sugar occurs.

As shown by irregularities in factory and laboratory work, this substance has been present in the beets of the Alameda Sugar Company, Alvarado, Cal., for the past five years, and for the past three years its disturbing influence has been very marked. In January of 1909, the author began experiments to search for some optically active non-sugar which would explain the results of observation made in the campaign of 1908, and was soon rewarded by obtaining from the evaporator thick juice a dextro-rotatory substance which was not precipitated by basic lead acetate in water solution and gave a dextro-rotation in acid, alkaline, and neutral solution.

This substance was first obtained from the evaporator thick juice, later from the molasses, and afterward from the evaporator condensation water produced during the concentration of the osmose syrup.

Throughout the inter-campaign all of the spare time was spent in extracting and experimenting with this substance, but at no time did the specimen obtained appear to be pure, and in quantity enough, to attempt an analysis to determine the composition of the rotatory substance. Naturally, small quantities had to be worked with, and after the extraction and numerous washings necessary to free it from the adhering substances there was very little left. A solution was obtained from one experiment which, when concentrated and then diluted to just fill a 200 mm. tube, gave a reading of 30° to the right. It has been extracted from the molasses of 1904, 1905, 1907, and 1908, and from the beet and factory products of 1909.

As obtained, the following properties have been ascribed to it :—

It may be considered as an acid, or a substance which, like sugar, can be combined with calcium or lead. The solutions which have contained it free from bases have been faintly acid to phenolphthalein, but this acid may not be the rotatory substance. It was found to be very difficult to free the solution from acetic acid.

It is, in a free condition, easily soluble in water, alcohol, and acetone, but insoluble in either.

The lead compound, produced by basic lead acetate is soluble in water and dilute alcohol and quite soluble in

strong methyl alcohol, but almost insoluble in ethyl alcohol of 85 per cent.

The calcium and sodium compounds are readily soluble in water and also in dilute alcohol, but practically insoluble in absolute alcohol. Much more soluble in strong methyl alcohol than in strong ethyl alcohol.

As obtained from the thick juice of 1908, and the evaporator condensation water from the osmosed syrup, it is not destroyed by heating with dilute mineral acids, neither is it destroyed by the usual inversion method of heating for five minutes at 68° C. with concentrated hydrochloric acid, but long heating in such acid renders it inactive. Strong acetic acid destroys it readily when heated on the water-bath at 70° C.

By heating on the water bath-with milk of llme it loses its optical activity entirely, but if slowly evaporated in slightly alkaline solution it does not lose this property, and when evaporated to dryness from a neutral solution it may be heated to 110° C. for hours without changing its rotatory power.

It is not volatile, but can be carried over from a dilute acid solution, by distilling with a current of steam.

It does not reduce Fehling's solution and is not destroyed by alcoholic fermentation.

No signs of crystalliisation have been observed, and in the nearest approach to purity that it has been obtained, it was of a light amber colour, in appearance resembling very closely light-coloured gum arabic, but completely soluble in absolute alcohol.

The lead compound, after thorough washing, is soluble in an excess of lead acetate. If, however, it is dried, it then becomes insoluble in lead acetate, but on boiling with water and decomposing with H_2S a dextro-rotatory solution is obtained, which is not destroyed by heating with strong hydrochloric acid.

The substance obtained directly from the beet is apparently more readily affected by acid than that obtained from molasses, or from the condensed water from evaporating osmose syrup.

My experience with this substance leads me to believe that either it exists in the beet as a complex, unstable compound, which readily breaks down into products of lower optical power and quite stable, or that we have orginally two closely allied substances, one of which readily changes and loses it power to rotate light, while the other is more stable and requires vigorous treatment to change its properties.

The fact that its lead compound is practically insoluble in strong alcohol affords a ready method for obtaining it directly from the beet. And the fact that this lead compound is readily soluble in dilute alcohol accounts for the agreement of water and alcohol digestions when made by the usual methods.

If finely grated beets are extracted with 90 per cent alcohol and basic lead acetate added to the clear solution thus obtained, there will be produced a yellowish white precipitate. If this procedure is carefully carried out, it will be found that the polarisation of the alcoholic solution before the addition of lead acetate will correspond very closely to the polarisation of the water digest made with the requisite amount of lead acetate. It will also be found that the polarisation of the alcoholic solution after the addition of the lead acetate and the proper correction for dilution is considerably lower than of the water digest. This, so far as I am aware, has been attributed to the precipitation of sugar by the lead acetate in alcoholic solution. A pure sugar solution, in the same strength of alcohol, will not yield a precipitate when lead acetate is added, unless a very large excess is used. In the case of the beet juice in alcohol, it is found that if the addition of the lead acetate is cautiously made and time allowed for the separation, a point will be reached when the further addition of the reagent does not cause further precipitation. If, at this point, the precipitate is filtered off and thoroughly washed with alcohol containing a little lead acetate and afterwards with water, then boiled with water and H_2S passed in, the lead is precipitated as sulphide, and after cooling and filtering a solution is obtained which turns the ray of light to the right. By the addition of alcohol and lead acetate to this solution a precipitate is again formed. If this is washed with alcohol and lead acetate until a 400 mm. tube, filled with the washings, gives a rotation so slight as to be scarcely definable, then the residue boiled with water and decomposed with H_2S, the solution obtained is dextro-rotatory and remains so after heating for five minutes with concentrated hydrochloric acid.

The difference between the polarisation of water digest and the alcohol digest, maintaining an alcoholic strength of 85 per cent, have generally been greater than the differences between the direct and inversion polarisations, and in my determinations I have not been able to obtain a quantitative separation which would agree with the difference between the water and alcohol digest, though in one carefully carried out test, in which an accumulation of several precipitates was used, the results were not far from the results obtained by inversion.

By carefully carrying out comparative estimations of the sugar in the beets and the various products of the factory, by the use of water solutions and alcoholic solutions of 85 per cent to 90 per cent, it has been shown that there is a continual diminishing of the differences between the polarisations of the water and alcoholic solutions, from the entrance of the beets to the factory until the juice has passed through all of the saturation stations, and that afterward there is not the increase in these differences that we should have, as these saturation juices are concentrated to fillmass. This has been shown also by the inversion method of estimating the sugar. The results of determinations made during the last campaign show differences ranging from nothing to as much as one and one-half per cent in the beets and beet juices, and averaging less for the diffusion juice than for the beets, while the differences in polarisations of water and alcohol solutions of the first saturation juices was seldom over two-tenths of 1 per cent. If after the defecation by lime there was no further loss of this dextro-rotatory substance, it should occur (owing to the concentration) in the final molasses in quantities indicating 2 or 3 per cent of sugar, but this has not been found to be the case, the average being only about six-tenths of 1 per cent.

As previously stated, this dextro-rotatory substance has been obtained from the evaporator condensation water when concentrating the osmosed syrup, and in the campaign of 1909 the vapours escaping from the first liming or defecation pan where condensed, and from these condensed vapours a dextro-rotatory substance was extracted. By greatly concentrating the condensation water from the evaporators, I was able to get it from this also, but in very small amounts. Especially interesting in connection with the water solution obtained from the condensation of the vapours from the lime pan was the fact that, as it was concentrated, it gradually became brown, and from an almost colourless solution it changed to a dark brown mass of the consistency and colour of beet molasses, and decomposed as it was concentrated on the water-bath, yielding a brown powder insoluble in water. In this respect, it conducted itself like the free acids obtained when extracting the first specimen of the dextro-rotatory substance from the evaporator thick juice. The presence of this dextro-rotatory substance in the vapours readily explains why we do not have the increased differences between the polarisations of water and alcoholic solutions of the thick syrup, fillmasses, and molasses that we should naturally expect to have by concentrating the thin juices. This may also explain a long-existing question. Why do we always have an apparent loss of sugar during the evaporation and pan boiling of sugar solutions?

The theory first advanced by different writers on this subject, as to the cause of the presence of this particular dextro-rotatory substance in the sugar beet, viz., the weather conditions of the past few years, does not appear

to be well grounded. From the properties thus far obtained, and a review of the various methods proposed by different analysts in their efforts to establish a uniform and correct method for estimating the sugar in the beet, we find good evidence to indicate that it has always been a constituent, and that the increased percentage in the beets of the present day is more than probable, largely the result of seed selection, although it may be that the quantity is altered by the weather conditions. During the campaign of 1909, it was found in beets from widely different localities, where seasonal and climatic conditions were entirely different. It was found in beets grown at sea-level and those grown at several thousand feet elevation, in beets grown without rain or irrigation, and in beets grown with both rain and irrigation. It has been found in beets that have had a second growth and have remained in the ground all winter. From all of these various conditions the differences have not varied materially more than from the beets taken from the same field at the same time. It thus appears that locality and climatic conditions are not the primary cause for the presence of this dextro-rotatory substance in the beets.

In conclusion, I wish to say that my experience has fully convinced me that the observations of Dr. Kopecky, and other chemists who have found differences between the polarisations by the direct and by the inversion methods, have been correct, and that the probable reason why these differences have not been greater in many cases, and why other chemists have failed to find any such differences has been due to the destructive action of the acetic acid liberated from the lead acetate by the hydrochloric acid, added for the inversion. Also, my work has shown that the discovery of Ing. Fr. Herles that there is a reduction of the polarisation of the beet juice and diffusion juice, when they are heated with lime, and also that it is possible to precipitate this substance by lead acetate in very strong alkaline solution, as with caustic lime and basic lead acetate in combination, is correct.

It is my intention to continue the study of this substance, and if possible to ultimately determine its composition.—*Journal of Industrial and Engineering Chemistry*, ii., No. 7.

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,*

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, &c.

By PERCY H. WALKER.

(Continued from p. 44).

Paint Materials.

Linseed Oil.

1. *Preparation of Sample.*—All tests are to be made on oil which has been filtered through paper at a temperature of between 15° and 30° C. immediately before weighing, with the exception of Tests No. 6, Turbidity; No. 7, Foots; No. 9, Moisture and Volatile Matter; and No. 10, Ash. The sample should be thoroughly agitated before the removal of a portion for filtration or analysis.

2. *Specific Gravity.*—Determine with a pyknometer, plummet, or hydrometer at 15·5° C.

3. *Viscosity.*—Use the Engler-Ubbelohde method, making the determination at 20° C.

4. *Flash Point, Open Cup.*—Set a nickel crucible 60 mm. in diameter at the top, 40 mm. in diameter at the bottom, and 60 mm. in height, in a hole in the middle of a sheet of asbestos board 200 mm. square. The bottom of the crucible should project about 25 mm. through the asbestos. Support the asbestos on a tripod and suspend a thermometer reading to 400° C. in degrees in the centre of the crucible, so that the lower end of the thermometer is 10 mm. from the bottom of the crucible. Then pour in the oil until its level is 15 mm. below the top of the crucible. Place a Bunsen burner below the crucible and regulate the size of flame so that the thermometer rises 9° a minute. As a test flame use an ordinary blowpipe attached to a gas tube. The flame should be about 6 mm. long. Begin testing when the temperature of the oil reaches 220° C., and test for every rise of 3°. In applying the test move the flame slowly across the entire width of the crucible immediately in front of the thermometer and 10 mm. above the surface of the oil. The flash-point is the lowest temperature at which the vapours above the oil flash and then go out.

5. *Fire-point.*—After noting the temperature at which the oil flashes continue the heating until the vapours catch fire and burn over the surface of the oil. The temperature at which this takes place is the fire-point. In determining the flash-point note the behaviour of the oil. It should not foam or crack on heating. Foaming and cracking are frequently caused by the presence of water.

6. *Turbidity.*—Note whether the oil is perfectly clear or not.

7. *Foots.*—Let a litre of the oil stand in a clear glass bottle for eight days, and then note the amount of sediment formed. The highest grades of oil show no turbidity or foots by this test. The claim is made that sometimes what would be called foots by the above method is due to the freezing out of fats of rather high melting-point. When a sufficient amount of the sample is available, heat one portion to 100° C. and set it aside for the determination of foots, together with a sample just as it is received. Note also the odour of the warm oil, rubbing it on the hands; a small amount of fish oil may be detected in this way.

8. *Break.*—Heat 50 cc. of the oil in a beaker to 300° C. Note whether the oil remains unchanged or "breaks"; that is, shows clots of a jelly-like consistency.

9. *Moisture and Volatile Matter.*—Heat about 5 grms. of oil in an oven at 105° for forty-five minutes; the loss in weight is considered as moisture. This determination is of course not exact, as there is some oxidation. When a more accurate determination is desired, perform the whole operation in an atmosphere of hydrogen.

10. *Ash.*—Burn about 20 grms. of oil in a porcelain dish and conduct the ashing at as low a temperature as possible. The best oil should contain only a trace of ash. An amount as large as 0·2 per cent would indicate an adulterated or boiled oil. Examine the ash for lead, manganese, and calcium.

11. *Drying on Glass.*—Coat glass plates 3 by 4 inches with the oils to be examined, expose to air and light, and note when the film ceases to be tacky. A good oil should dry to an elastic coherent film in three days. Varying conditions of light, temperature, and moisture have such an influence on drying tests that for comparison of one linseed oil with others all samples must be run at the same time.

12. *Drying on Lead Monoxide.*—Livache's test calls for precipitated lead, but litharge gives equally good results. Spread about 5 grms. of litharge over the flat bottom of an aluminium dish 2·5 inches in diameter and five-eighths of an inch high; weigh the dish and the litharge; distribute as evenly as possible over the litharge 0·5 to 0·7 grm. of the oil, weigh exactly, expose to the air and light for ninety-six hours, weigh again, and calculate the gain in weight to percentage based on the original weight of the oil used.

13. *Acid Number.*—Weigh 10 grms. of oil in a 200 cc. Erlenmeyer flask, add 50 cc. of neutral alcohol, connect with a reflux air condenser, and heat on a steam-bath for half-an-hour. Remove from the bath, cool, add phenolphthalein, and titrate the free acid with fifth-normal sodium hydroxide. Calculate as the acid number (milligrms. of potassium hydroxide to 1 grm. of oil). The acid number varies with the age of the oil, and should be less than 8, though when the oil is refined with sulphuric acid it may show a higher acid number. Test for sulphuric acid.

* *Bulletin* No. 109, Revised, U.S. Department of Agriculture, Bureau of Chemistry.

14. *Saponification Number.*—Weigh from 2 to 3 grms. of oil in a 200 cc. Erlenmeyer flask, add 30 cc. of a half-normal alcoholic solution of potassium hydroxide, connect with a reflux air condenser, heat on a steam-bath for an hour, then titrate with half-normal sulphuric acid, using phenolphthalein as indicator. Always run two blanks with the alcoholic potash. From the difference between the number of cubic centimetres of acid required by the blanks and the determinations, calculate the saponification number (milligrms. of potassium hydroxide to 1 grm. of oil). The saponification number should be about 190.

15. *Unsaponifiable Matter.*—As the saponification varies somewhat in pure oil, it is sometimes advisable to make a direct determination of unsaponifiable matter. Saponify from 5 to 10 grms. of oil with alcoholic potassium hydroxide (200 cc. of a half-normal solution) for an hour on a steam-bath, using a reflux condenser. Then remove the condenser and evaporate the alcohol as completely as possible; dissolve the soap in 75 cc. of water, transfer to a separatory funnel, cool, shake out with two portions of 50 cc. each of gasoline distilled between 35° and 50° C., wash the gasoline twice with water, evaporate the gasoline, and weigh the unsaponifiable matter, which in raw linseed oil should be below 1·5 per cent; in boiled oil it is somewhat higher, but should be below 2·5 per cent.

16. *Iodine Number.*—Weigh in a small glass capsule from 0·2 to 0·25 grm. of oil, transfer to a 350 cc. bottle having a well-ground stopper; dissolve the oil in 10 cc. of chloroform, and add 30 cc. of Hanus solution; let it stand with occasional shaking for one hour, add 20 cc. of a 10 per cent solution of potassium iodide and 150 cc. of water, and titrate with standard sodium thiosulphate, using starch as indicator. Blanks must be run each time. From the difference between the amounts of sodium thiosulphate required by the blanks and the determination, calculate the iodine number (centigrms. of iodine to 1 grm. of oil). The iodine number of raw linseed oil varies from 175 to 193, though Gill states that a pure raw oil may give a value as low as 160. Boiled oil may be very much lower.

Make the Hanus solution by dissolving 13·2 grms. of iodine in 1000 cc. of glacial acetic acid which will not reduce chromic acid, and adding 3 cc. of bromine.

17. *Rosin or Rosin Oil (Liebermann-Storch Test).*—To 20 grms. of oil add 50 cc. of alcohol, heat on a steam-bath for fifteen minutes, cool, decant the alcohol, evaporate to dryness, add 5 cc. of acetic anhydride, warm, cool, draw off the acetic anhydride, and add a drop of sulphuric acid, 1·53 specific gravity. Rosin or rosin oil gives a fugitive violet color.

Spirits of Turpentine.

(NOTE.—If wood turpentine has been carefully refined, it will comply with all the tests given for spirits of turpentine, but it can almost invariably be distinguished from the latter by its characteristic odour).

1. *Colour.*—The best quality of spirits of turpentine should be water white.

2. *Specific Gravity.*—Determine the specific gravity with a pyknometer, plummet, or hydrometer at 15·5° C. Pure gum turpentine should have a density between 0·862 and 0·875. Wood turpentine may, however, range from 0·860 to 0·910 or even higher.

3. *Distillation.*—Connect a distilling flask of 150 cc. capacity with a condenser having a thermometer. Introduce 100 cc. of turpentine and heat with a Bunsen burner. The initial boiling-point should be about 156° C., and 95 per cent should distil over between 153·5 and 165·5 C.

4. *Residue on Evaporation.*—Evaporate 10 grms. on the steam-bath; the residue should be less than 2 per cent.

5. *Refractive Index.*—Determine with a Zeiss direct reading refractometer at 20° C. The index of refraction for gum turpentine should be from 1·4690 to 1·4740; for wood turpentine, 1·4685 to 1·5150.

6. *Action of Sulphuric Acid (Polymerisation).*—Measure 6 cc. of turpentine in a stoppered thin-walled tube graduated to 0·1 cc. (carbon tubes). Place the tube in cold water and pour in slowly a mixture of four parts of strong sulphuric acid and one part of fuming sulphuric acid. Add the acid slowly, and avoid an excessive rise in temperature. Shake the tube so as to mix the turpentine and the acid, add finally about 20 cc. of the acid, stopper the tube, mix thoroughly, cool, allow to stand thirty minutes, and note the volume of unpolymerised oil that collects on top of the acid layer. Then let stand for eighteen hours, and again note the volume. A pure turpentine should show less than 0·3 cc. unpolymerised at the end of thirty minutes, and less than 0·5 cc. after eighteen hours.

This method will indicate gross adulteration, but will not detect admixtures of very small amounts of mineral oil. Donk has perfected a method which determines the presence of as little as 1 per cent of mineral oil in turpentine. This method is as follows:—

Sulphuric acid of thirty-eight times the normal strength (101·5 per cent) is prepared by mixing very strong sulphuric acid with fuming sulphuric acid. It must be determined by titration that this reagent is of the exact strength required, for with 37·5 times normal acid (100 per cent) the turpentine is not completely destroyed, and with acid stronger than 101·5 per cent the amount of mineral oil dissolved becomes excessive.

Place about 25 cc. of the special sulphuric acid in a flask having a narrow graduated neck (a Babcock bottle does very well), cool in ice water, add 5 cc. of the turpentine to be tested and cool the flask again, shaking it carefully and avoiding any excessive rise in temperature by frequent cooling. The flask should never be too hot to hold in the palm of the hand. Then place it in a bath of cold water and heat the bath at such a rate that in about five minutes the temperature will be 65° C. During the heating shake the bottle about every fifty seconds, finally shaking very thoroughly so as to insure the contact of every particle of the sample with the acid. Cool to room temperature and add ordinary strong sulphuric acid in sufficient amount to bring the unpolymerised liquid up in the graduated neck. Let stand over night or whirl in a centrifuge, and read the volume on the neck.

Pure turpentine should leave a residue of not over 0·04 cc., which is not limpid and which has a refractive index of not less than 1·500.

If the unpolymerised residue is 0·04 cc. or less, mineral oil may be assumed to be absent. If the residue is greater, calculate from it the percentage of mineral oil present. This will be, of course, only approximate, for there is some residue from pure turpentine, and some mineral oil is dissolved by the acid; but for all practical purposes it may be assumed that the errors balance one another, and hence it is not advisable to apply any correction.

7. *Spot Test.*—Place a drop on filter-paper and allow it to dry at room temperature; it should leave no stain.

8. *Flash-point.*—Support a crucible, such as is used in determining the flash-point of linseed oil, in a vessel of water at 15° to 20° C.; the water should cover about two-thirds of the crucible. Fill the crucible to within about 2 cm. of the top with turpentine, insert a thermometer, and heat the water-bath slowly, 1° per minute. Begin at 37° and test for the flash at each rise of 0·5°. The turpentine should not flash under 40·5° C.

(To be continued).

Red Lines for a Balance Scale.—C. M. Clark.—Having occasion recently to purchase a balance, it occurred to me that, as colour contrast is an aid to vision, it might be of assistance in reading the variations of the needle on a balance scale, and I therefore instructed the makers to equip the balance with an ivory scale having *red* lines instead of the usual black ones. This was done, and the result has justified my anticipations. The contrast between the black needle and the red lines on a white background is restful and pleasing to the eyes, and enables a close weighing with less eye-strain than with the black lines. No extra expense was incurred in making the change from black lines to red, and I would recommend such innovation to those contemplating the purchase of a balance.—*Journal of the American Chemical Society*, xxxii., No. 7.

NOTICES OF BOOKS.

Qualitative Chemical Analysis, Organic and Inorganic. By F. Mollwo Perkin, Ph.D. Third Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1910.

This book, in which theory and practice are excellently blended, has won for itself the appreciation of all teachers and students who have been fortunate enough to come across it, and the third edition will no doubt be as heartily welcomed as its predecessors. Some few additions have been made to the text, which has also been thoroughly revised. The reactions of the more important of the rarer elements are now included, and a new section on ethereal salts has been added. The organic part of the book is particularly full, and students who work carefully through it should get a thorough knowledge of practical organic chemistry and a good acquaintance with the reactions of the commoner organic compounds.

Lead Smelting. Special Report on Dangerous or Injurious Processes in the Smelting of Materials containing Lead and in the Manufacture of Red and Orange Lead and Flaked Litharge." By Edgar L. Collis, M.B. London: Wyman and Sons, Ltd. Edinburgh: Oliver and Boyd. Dublin: E. Ponsonby. 1910.

This report contains statistics of the cases of plumbism which have occurred among workers engaged in the smelting of metals from January, 1904, to December, 1909, with descriptions of the processes employed in lead and zinc smelting, and in the preparation of the oxides of lead. Recommendations of the precautions to be observed in the smelting of materials containing lead, and the manufacture of red and orange lead and flaked litharge, are given in detail, and the German and French regulations in force at the present time are also included for the sake of comparison.

Le Jubilé Académique de Monsieur L. P. Cailletet. ("The Academic Jubilee of M. L. P. Cailletet"). January 18, 1910.

To celebrate the twenty-fifth anniversary of M. Cailletet's admission to the Académie des Sciences this small volume has been issued. It contains a short biography of the great physicist with portraits, and an account of the banquet which followed the bestowal upon M. Cailletet of the medal struck in honour of the occasion. A chronological list of the articles he has published concludes the volume, which forms a fitting reminder of the great services he has rendered to science and of the cordial respect and admiration of his colleagues.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Notes.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cl., No. 19, May 9, 1910.

Magnetic Analysis of some Chromophoric Groups.—Paul Pascal.—The magnetic properties of a molecule are dependent upon its structure; thus a double bond always diminishes diamagnetism. Applying magnetic analysis to the study of dye-stuffs, the author finds that there is a connection between the possession of a strongly marked colour and a quinonic structure, at any rate in substances with an oxygen function. The quinone formation is often accompanied by phenolic tautomerism, especially in the cold, if the substance is not strongly coloured. On the other hand, in amino dyes, in which the nitrogen is not a constituent element of a closed chain in ordinary conditions, a quinonic tautomer does not appear to exist.

Chemical Effects of Ultra-violet Rays on Gases.—Daniel Berthelot and Henri Gaudechon.—The ultra-violet rays produced by a quartz mercury lamp cause the polymerisation of acetylene, both when it is alone and when hydrogen and nitrogen are mixed with it, a yellow solid deposit being formed. From ethylene a polymer in the form of a waxy liquid is produced; this polymer, which has a rancid smell, recalls caprylene. Mixtures of acetylene and ethylene give the same two products. From cyanogen paracyanogen is rapidly produced, and small quantities of ozone can be obtained from oxygen.

Some Trialkylacetonaphthones and their Decomposition by Sodamide.—V. Volmar.—When the trialkylacetonaphthones are treated with sodamide they are split up, the α-isomers undergoing an incomplete reaction; thus from α-trimethylacetophenone pivalic amide and naphthalene are formed. In the case of the β-isomers the reaction is complete and the products are different, only small quantities of pivalic amide and naphthalene are obtained, but, on the other hand, there is a good yield of naphthoic amide.

Action of Thionyl Chloride on Mixed Organo-magnesium Compounds.—V. Grignard and L. Zorn.—With aromatic organo-magnesium compounds thionyl chloride yields sulphinones, the two atoms of chlorine being replaced by organic radicals:—

$$SOCl_2 + 2RMgX = 2MgXCl + SO{<}^{R}_{R}.$$

With aliphatic organo-magnesium compounds the reaction goes further, thus—

$$SOCl_2 + 3RMgX = 2MgXCl + {}^{R}_{R}{>}S{<}^{R}_{OMgX}.$$

In the latter case the sulphonium complex is not stable, but may be decomposed according to either of the following equations:—

$$\text{(i.)}\ {}^{R}_{R}{>}S{<}^{R}_{OMgX} = {}^{R}_{R}{>}S + ROMgX;$$

$$\text{(ii.)}\ {}^{R}_{R}{>}S{<}^{C_nH_{2n+1}}_{OMgX} = {}^{R}_{R}{>}S + C_nH_{2n} + MgXOH.$$

Thus an organic sulphide is obtained together with either an alcohol or an ethylenic hydrocarbon.

Chloranthranilic Ethers and their Condensation with Nitrosobenzene.—P. Freundler.—When methylanthranilate is chlorinated in the cold both the dichlor- and the monochlor-derivatives are obtained. The latter condenses with nitrosobenzene at the ordinary temperature, yielding a yellow product fusing at 137°, and azoxy benzene. The formula of this yellow substance is $C_{14}H_{11}N_2O_3Cl$, and thus it differs from chlorobenzene-azobenzoic ether by one atom of oxygen. Its formation is represented by the equation—

$$3C_6H_5NO + H_2N.C_6H_3Cl.CO_2CH_3 = = C_6H_5.N_2O.C_6H_5 + C_{14}H_{11}N_2O_3Cl + H_2O.$$

It is a feeble base, and contains an ether salt group. When saponified with warm alcoholic soda it yields a yellowish brown acid.

Action of Dehydrating Agents on α-Glycols.—M. Tiffeneau.—Acetic anhydride converts primary tertiary α-glycols into vinylic acetates:—

$$RR'COH{-}CH_2OH + (CH_3CO)_2O = = RR'C{=}CH(OCOCH_3) + CH_3CO_2H.$$

Disecondary anethol glycol with dehydrating agents yields anisic acetone—

$$OCH_3{-}C_6H_4{-}CHOH{-}CHOH{-}CH_3 \xrightarrow{-H_2O} OCH_3{-}C_6H_4{-}CH_2{-}CO{-}CH_3.$$

No. 20, May 17, 1910.

General Method of Preparing Thiols from Alcohols by Catalysis.—Paul Sabatier and A. Mailhe.—With

alcohols thoria yields thorianates which are decomposed by heat, giving hydrocarbons and regenerating thoria. If an acid were added it seemed probable that an ether salt of the acid might be formed. Thus—

$$ThO(OC_nH_{2n+1})_2 + 2AH = 2(AC_nH_{2n+1}) + ThO_2 + H_2O.$$

Thus if sulphuretted hydrogen were used as the acid thiols would be formed. This prediction has been verified, and the authors have prepared many thiols directly from the corresponding alcohols. The yield is good when the thiol is not too volatile, and can readily be condensed. Thiophenols can be prepared by passing a mixture of vapours of phenol and sulphuretted hydrogen over thoria.

Action of Silent Discharge on Ethyl Aldehyde in Presence of Hydrogen.—A. Besson and L. Fournier.—When ethyl aldehyde is subjected to the silent discharge in presence of hydrogen the condensed products consist of water, acids (acetic and its homologues), and ketonic substances. The formation of ketones and diketones can be explained by a very simple mechanism:—

$2CH_3CHO = 2H + CO + CH_3COCH_3$, propanone.
$3CH_3CHO = 4H + 2CO + C_2H_5COCH_3$, butanone.
$2CH_3CHO = 2H + CH_3CO—COCH_3$, diacetyl.

The acids are formed according to the following equations:—

$2CH_3CHO = C_2H_4 + CH_3CO_2H$, acetic acid.
$4CH_3CHO = C_2H_4 + 2C_2H_5CO_2H$, propionic acid.

According to the experimental conditions one or other of these reactions may predominate. Water is formed by the condensation of the ketones with formation of mesityl oxide, phorone, and higher homologues, or by a more deep-seated destruction of the molecule:—$CH_3CHO = H_2O + C_2H_2$.

Synthesis of Aromatic Nitriles.—F. Bodroux and F. Taboury.—Nitriles of formula $C_6H_5—CR_2—CN$ can be prepared from benzyl cyanide by the following reactions:—

$$C_6H_5—CH_2—CN + 2Na—NH_2 = 2NH_3 + C_6H_5—CNa_2—CN$$
$$C_6H_5—CNa_2—CN + 2R—X = 2NaX + C_6H_5—CR_2—CN.$$

The authors have thus prepared 2-ethyl 2-phenyl butane nitrile and 2-propyl-2-phenyl pentane nitrile.

Action of Hydracids on Glycidic Ethers.—Georges Darzens.—Hydrochloric acid gives with $\beta\beta$-dimethylglycidic ether α-oxy-β-chlorisovalerianic ether. It is a crystalline substance, from which the dimethyl glycidic ether can readily be obtained by the action of sodium ethylate. When saponified with soda it is not possible to prepare the free acid, because of its instability in alkaline solution and its immediate transformation into isobutylic aldehyde. The action of hydrochloric acid on trimethylglycidic ether gives the corresponding ether, and similar results are obtained with hydrobromic acid. In all these reactions it is important to operate in absence of any trace of water. Hydriodic acid acts quite differently, the product with dimethylglycidic ether being dimethyl acrylic acid.

Two New Isomers of Stearolic Acid.—A. Arnaud and S. Posternak.—The dihydriodic derivative of stearolic acid gives on reduction with zinc and acetic acid stearic acid, and on decomposition with alcoholic potash a complex mixture which contains the original stearolic acid and also two new isomers with the triple bond displaced to the next carbons on the left and right respectively. The separation of the two isomers is effected by converting them into diiodo derivatives, and then subjecting these to fractional crystallisation. These reactions are not peculiar to stearolic acid, but apply also to other acids of the same series.

Hexahydrophenylglycolic Acid.—Marcel Godchot and Jules Frezouls.—This new compound can be prepared from hexahydrobenzoic aldehyde, which combines with hydrocyanic acid to give hexahydrophenylglycolic nitrile, from which the acid is obtained by saponification. The acid crystallises in prismatic needles which are slightly soluble in water; melting-point 130—131°. It is very soluble in ether, alcohol, and acetone. Since it possesses an asymmetric carbon atom it should yield active isomers, which the authors intend to prepare and investigate.

New Method of Determining the Three Methylamines and Ammonia.—J. Bertheaume.—Bresler's method of determining trimethylamines in presence of ammonia is unsatisfactory, because it depends upon the difference of solubility of the sulphates of the bases in alcohol, and this difference is only very small. A more accurate method which the author has worked out depends upon the action of chloroform on the chlorhydrates. Those of di- and trimethylamine are soluble, and they may be separated by preparing the periodides; the periodide of trimethylamine is insoluble, while that of dimethylamine is soluble. Ammonia and monomethylamine are insoluble in chloroform, and after the residue has been lixiviated with warm water the two may be separated by François's method.

MISCELLANEOUS.

City and Guilds of London Institute.—At a meeting of the Council of the City and Guilds of London Institute held on July 20th the diploma of "Associate of the City and Guilds of London Institute" was awarded to the following matriculated third year students of the Central Technical College who have completed a full course of instruction as prescribed by the Council:—Civil and Mechanical Engineering (50)—W. E. Bullock (awarded Bramwell Medal), H. R. Askew, H. G. Bambridge, R. E. Barton, R. O. Beit, C. St. J. Bird, M. A. Bulloch, R. Burton, E. R. A. Campbell, A. B. Chester, E. V. M. Crofton, C. J. Davis, W. R. Deuchar, A. P. Dicksee, D. M. Dinwiddie, C. L. Druitt, H. F. V. Ellison, E. P. Elworthy, W. J. Forsyth, F. R. Freeman, J. C. Gibson, A. C. Hartley, C. G. Hawes, E. S. Hoare, E. W. C. Jones, L. C. Kemp, L. A. E. Langlois, R. A. Mack, H. J. Masters, G. S. Mitchell, W. C. Mitchell, E. Moore, M. L. J. Morau, T. E. de Morsier, A. W. B. Pallister, P. G. Pappanicolaou, L. M. Paterson, H. G. Peake, G. T. Pound, J. H. F. Raper, G. A. N. Raymond, H. B. Richards, J. Richardson, H. G. Salmond, J. L. Sanders, E. H. G. Tomblings, D. C. W. Tonkin, A. D. Turner, N. L. Wallis, T. R. Young. Electrical Engineering (25)—J. D. Peattie (Awarded Siemens Memorial Medal and Premium), M. de Angelis, W. S. G. Baker, W. Barrs, P. R. Blamey, H. Clark, H. M. Dunkerley, D. H. Green, W. C. Griffith, G. E. W. Hitchcock, A. E. D. Kennard, G. Lambert, A. W. M. Mawby, P. A. McGee, D. J. McHatton, R. F. Niven, N. J. Perryman, L. C. Pocock, F. C. L. Racker, N. N. Roy, L. L. Ruderman, J. McL. Thornton, G. H. Tilly, F. J. Vinsen, G. Watts. Chemistry (5)—H. L. Armstrong, A. J. Daish, W. H. Franklin, F. W. Jackson, C. S. Mummery. In addition to the above, Certificates have been awarded to 19 matriculated third year students who have completed a full course of instruction at the Central Technical College, and to 56 students who have completed a full course of instrucrion at the Technical College, Finsbury.

NOTES AND QUERIES.

"*" Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Vacation Work.— I should be greatly obliged for information as to whether there is a possibility of working in organic chemistry during the months of August and September, in London, either in a public or private laboratory.—Dr. R. V.

THE CHEMICAL NEWS.

Vol. CII., No. 2645.

RESULTS ON THE EXAMINATION OF THE AVOCADO PEAR.

By J. S. JAMIESON, F.I.C.

The edible part of the fruit is a sweetish substance with semi-solid consistency, and largely used as a condiment.

The analysis was first made on the original fruit, and afterwards on the fruit dried at 100° C.

	Sample dried at 105° C.	Original sample.
	Per cent.	Per cent.
Ether extract ..	58·60	19·63
Woody fibre ..	14·75	4·94
Sugar	3·23	1·08
Protein	17·06	5·71
Ash	6·10	2·04
Water	—	66·92

The ether extract was a greenish liquid containing about 4 per cent of resinous matter which was dissolved by alcohol, leaving the oil in a pure state; this oil had the appearance of oil of Bergamot.

The following are the constants of the purified oil:—

Koettstorfer value	0·207
Iodine value	29·90
Zeiss butyrometer	65 at 20° C.
Oleorefractometer	+4

The following is the result of an analysis made by Wiley (see "Foods and their Adulterations," by Wiley, p. 344):—

	Per cent.
Water	81·10
Ether extract (fat)	10·20
Protein	1·00
Starch and sugar	6·80
Ash	0·90

The composition of the American variety seems very different from the Natal species, and appears to be rather remarkable considering they are of the same species.

Government Laboratory, Durban, S.A.,
June 29, 1910.

THE CHANGE OF CARBON DISULPHIDE INTO A GASEOUS PRODUCT CONDENSABLE AND EXPLOSIVE NEAR THE TEMPERATURE OF LIQUID AIR.

By Sir JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S.,
Jacksonian Professor in the University of Cambridge,
and
HUMPHREY OWEN JONES, M.A., D.Sc.,
Jacksonian Demonstrator in the Universiity of Cambridge.

In a note communicated to the Society recently we described the preparation and properties of a polymeric form of carbon monosulphide. It was to be expected that carbon monosulphide would be a gas boiling at about −130° C.; yet the interaction of thiophosgene and nickel carbonyl at temperatures as low as −20° C. resulted in the formation of a polymeride, while when the same reaction was tried at −80° C. no change could be observed in the course of several hours.

The decomposition of carbon disulphide by light, studied by Sidot, also produces a polymeric form of carbon monosulphide, and we have shown that when this change is effected at −80° C. by means of ultra-violet light a similar substance is apparently formed.

It seemed possible that carbon disulphide vapour at low pressures might be decomposed under the influence of the silent electric discharge or of the ultra-vlolet radiation associated with it. The conditions might then be favourable to the stability of the mono-molecular carbon monosulphide, provided a rapid current of the hypothetical vapour could be passed through the discharged tube; as the presumably unstable gaseous carbon monosulphide might remain unpolymerised, in the presence of sulphur and a large excess of carbon disulphide vapour, for a sufficient time to allow it to be condensed together with the unchanged carbon disulphide when cooled to the temperature of liquid air.

This anticipation was experimentally examined in the following way:—A bulb containing carbon disulphide was sealed on to an annular vessel through which the silent electric discharge could be passed, and the latter was sealed to a U-tube made of quill tubing and a bulb containing charcoal. While the bulb containing carbon disulphide was immersed in liquid air, the rest of the apparatus was thoroughly dried and cleaned by heating and exhausting by means of a good air-pump; it was then sealed off and the charcoal bulb cooled in liquid air. The apparatus made solely of glass was now so thoroughly exhausted that no discharge would pass through the "ozoniser." The bulb containing carbon disulphide was now transferred from liquid air to a paste of solid carbon dioxide and ether, and thus maintained at a temperature of −80° C. In this way a rapid stream of carbon disulphide vapour at a steady pressure of about 1 mm. passed through the "ozoniser" and the U-tube, and was condensed in the charcoal bulb. On cooling the U-tube in liquid air, the carbon disulphide vapour was condensed and solidified as a white crystalline solid ring, When, after five or ten minutes, the U-tube was removed from the liquid air and allowed to rise in temperature, the carbon disulphide melted and quickly evaporated into the charcoal bulb, leaving no residue. The charcoal vacuum was maintained throughout the experiment, in order to ensure the absence of pressure due to any permanent gas.

While the U-tube was cooled in liquid air, the silent discharge was caused to pass through the vapour in the "ozoniser," causing a bluish light to fill the vessel: the discharge could be stopped at once by cooling the carbon disulphide bulb in liquid air. After the discharge had been allowed to pass for five minutes, a faint brown ring was noticed in the U-tube about a centimetre above the level of the surface of the liquid air. The liquid air was then removed, and the temperature of the U-tube allowed to rise, when a flash of light, accompanied by a detonation, was observed, and the surface of of the U-tube was fouud to be partly covered with a dark brown deposit. The detonation was usually gentle, but was sometimes so violent that the tube was shattered. A similar explosion may take place in the charcoal condenser.

When the conditions are arranged so that the temperature gradient in the U-tube is steep, as it is when the vacuum' vessel surrounding it is filled to the top with liquid air, then the transformation may take place during the condensation, and no flash will occur when the temperature is allowed to rise. If, on the other hand, the temperature gradient is not steep, as when the vacuum vessel is only half filled with liquid air, the flash can always be observed in a darkened room and frequently also in daylight.

On examination, the interior of the "ozoniser" is found to be partly covered with a thin brownish deposit which consists partly of sulphur and can be dissolved away by carbon disulphide. When the potential of the discharge was increased until sparks passed through the air outside the "ozoniser," then its inside surface became coated with a brown deposit similar in appearance to that which was found in the U-tube.

In order to show that the brown deposit in the U-tube was due to the change of a gaseous substance, a plug of

asbestos or of cotton-wool, from 2 to 6 cm. in length, was placed in a wider part of the tube between the "ozoniser" and the U-tube. The flash of light, detonation, and formation of a brown deposit took place in the U-tube as before.

The phenomena as described above were also observed when an "ozoniser" with outside terminals of tin-foil was completely immersed in paraffin oil; this excludes the possibility of ozone being formed in the apparatus through air leakage due to any piercing of the glass by the electric discharge.

The apparatus was slightly modified so that the bulb containing carbon disulphide and also the U-tube could be detached and weighed, so as to obtain a rough estimate of the ratio between the weight of carbon disulphide passed through the "ozoniser" and the weight of the brown solid produced. In a large number of experiments with different forms of "ozoniser," each lasting from ten to thirty minutes, it was found that the ratio of the weights varied from 9 to 1 to 16 to 1. In each experiment from 20 to 30 mgrms. of carbon disulphide were evaporated.

The properties of the brown deposit formed in the U-tube, in so far as we have been able to examine them with the small amount of material which can be obtained in this way, are almost identical with these of the polymeric form of carbon monosulphide which we have described. The deposit contains carbon and sulphur, is soluble in concentrated sulphuric acid to a brown-purple solution, and in alcoholic caustic soda to a very dark brown solution from which acids precipitate it apparently unchanged.

It would therefore seem fair to conclude that carbon disulphide vapour has been decomposed by the silent electric discharge into sulphur and gaseous carbon monosulphide, that the latter has been condensed with the unchanged carbon disulphide at the temperature of liquid air, and that it polymerises at a slightly higher temperature with explosive violence to the brown solid. In any case the experiments seem to suggest the existence of a new volatile sulphide of carbon.

If the above suggestion is correct, then the vapour of carbon disulphide is finally converted into two solids, and its pressure should disappear; but so long as only gaseous carbon monosulphide is formed there should be no change of pressure. An "ozoniser" sealed to a mercury manometer was carefully cleaned by heating under exhaustion, and pure dry carbon disulphide vapour was admitted to a pressure of 15 mm., the apparatus sealed and the silent discharge passed through the vapour. In about fifteen minutes the pressure had fallen to 1 mm., at which value it remained. This shows that carbon disulphide has been converted into non-volatile products, either sulphur and polymerised carbon monosulphide or the latter along with free carbon.

The influence of heat on the rapidly moving gaseous mixture which came from the "ozoniser" was now examined, and it was found that the gas in the presence of excess of carbon disulphide vapour was surprisingly stable. Some of the gas was still present after passing the product through a tube immersed in boiling sulphur or even through a short length of red-hot tube, but it was completely destroyed after passing through 10 cm. of red-hot tube loosely packed with asbestos.

This unexpected stability at high temperatures corresponds with a character of endothermic bodies and suggests that the gas only becomes highly unstable when condensed, and that it might be preserved for some time in the presence of excess of carbon disulphide vapour at low pressures. In order so test this possibility, a litre flask with a delivery tube leading nearly to the bottom was introduced between the "ozoniser" and the U-tube and the apparatus made solely of glass exhausted as before. When the discharge had been passing for about ten minutes the explosive gas could be detected by the flash got in the usual way in the small U-tube cooled in liquid air. A small portion of the surface of the flask was now cooled by the application of a sponge containing liquid air, when a deposit of solid carbon disulphide was soon formed. On removing the cooling agent this carbon disulphide soon melted to a *coloured* liquid and quickly evaporated, leaving a brown deposit. After a few minutes the flask being again full of gas the charcoal bulb was shut off from the apparatus by means of a tap and the discharge stopped; thus the large flask was left filled with carbon disulphide vapour containing about 10 per cent of the new gaseous body if assumed to be carbon monosulphide. At different intervals in separate experiments the cooling was repeated, and it was found that the deposit of carbon disulphide was coloured and left a residue at any time less than thirty seconds after the discharge had been stopped, but was colourless and left no residue when a minute had elapsed. After several experiments had been made, the general surface of the flask was covered with a visible brown deposit. It therefore appears that the gaseous sulphide of carbon polymerises rapidly at the ordinary temperature, even at low pressures and in the presence of a large excess of carbon disulphide. It may be possible to separate the new body from the admixed carbon disulphide by fractional distillation at very low temperatures. We hope to continue this investigation and to extend a similar study to other bodies.—*Proceedings of the Royal Society*, A, lxxxiii., p. 526.

FURTHER STUDIES OF THE REACTIONS OF LIME-SULPHUR SOLUTION AND ALKALI WATERS ON LEAD ARSENATES.

By C. E. BRADLEY and H. V. TARTAR.

It was shown by us that only very small quantities of arsenic were rendered soluble on mixing a neutral lead arsenate and commercial lime-sulphur in a combined spray (*Journ. Ind. Eng. Chem.*, i., 610). More recently, we have noticed that the residue from the mixture of an acid arsenate was much darker in colour than that from the neutral, indicating that considerable decomposition or interreaction had taken place in the former instance. It was thought advisable therefore to make a comparative study of the reactions taking place and the product formed when either the acid or neutral arsenate of lead is mixed with the lime-sulphur solution under spraying conditions.

A sample of Niagara lime-sulphur having a specific gravity of 32° B. was selected for the tests. Bean's ortho arsenate of lead was taken as a representative of the neutral, and Hemingway's arsenate as a type of the acid arsenate. Analysis in the laboratory of the Agricultural Experiment Station, Corvallis, Oregon, had shown these arsenates to have the following composition :—

Composition of Lead Arsenates.

	Hemingway's. Per cent.	Bean's. Per cent.
Moisture	32·46	41·68
Total PbO	42·64	42·19
Total As_2O_5..	21·45	13·47
Soluble As_2O_5	0·31	0·10
Soluble impurities ..	0·93	1·60
Total..	97·48	98·94

The arsenates were in each instance added in the proportion of 4 pounds of the moist arsenate to one hundred gallons of the lime-sulphur diluted 1 to 30. The mixtures were agitated occasionally for twenty-four hours, then filtered, and the residue washed and dried at 80° C., then at 100°. The residue from the acid arsenate was very dark in colour from the lead sulphide present, while that from the neutral was grey, indicating but slight decomposition. A partial analysis of the filtrate from each arsenate gave results as follows, a blank consisting of untreated lime-sulphur being run for comparison :—

Composition of the Lime-sulphur Solution before and after Addition of Lead Arsenate.

	Black lime-sulphur.	Grms. per 1000 cc. filtrate from acid arsenate and lime-sulphur.	Filtrate from neutral arsenate and lime-sulphur.
Total S ..	10·750	10·256	—
Total CaO	4·380	4·060	—
As_2O_5 ..	—	0·095	0·012

The above results indicate that eight times as much arsenic is rendered soluble from the acid arsenate as from the neutral, or calculated to the original material this would be equivalent to 0·25 per cent of soluble As_2O_5 from the neutral and 1·98 per cent from the acid. Distinct losses of sulphur and lime have also taken place in the acid arsenate mixture, and it is evident that there is a mutual decomposition when lead acid arsenate is mixed with the lime-sulphur solution.

Analysis of the dried residues give further evidence of the breaking down of the acid arsenate under these conditions :—

Analysis of the Residue from the Mixture of Lime-sulphur and Lead Arsenate.

	Neutral arsenate residue. Per cent.	Acid arsenate residue. Per cent.
Free S ..	0·70	20·80
PbS . ..	1·47	14·80
CaO.. ..	—	10·40

Sulphur was determined by extracting the dry residue with CS_2; the lead sulphide by extracting the remaining residue with HNO_3 1 : 10; the lime by precipitation as oxalate after removing lead and arsenic with hydrogen sulphide.

A study of the reactions involved in the above mixtures indicates that there is a partial interchange of the lime and lead resulting in the formation of calcium arsenate and lead sulphide respectively, free sulphur being at the same time deposited. The soluble arsenic is then derived from partial solution of the calcium arsenate thus formed. Sulphides of arsenic are not formed, as these sulphides are soluble in the alkaline lime-sulphur forming sulpho salts, and sulpho salts are not present in the solution. The reactions as shown above are much more pronounced with the acid than with the neutral arsenate, and it is therefore advisable to employ the neutral form when desiring to combine lime-sulphur and lead arsenate.

Having found that the *alkaline* lime-sulphur solution reacts quite readily with the *acid* lead arsenate, the tests were extended to determine the comparative solvent action of alkaline and saline waters on these arsenates.

Haedden has stated (*Bull.* 131, Col. Exp. Sta.) that lead arsenate is more soluble in waters containing alkali salts than in normal water. In the tests which are reported in the succeeding table a quantity of the moist arsenate, equivalent to 10 grms. of the dry arsenate, was treated in each case with 2 litres of solution, except in case of the CO_2 test, in which 2 grms. of the moist arsenate were used. The solutions were kept at room temperature (about 17° C.) for twenty-four hours with occasional shaking,, then filtered, and the filtrate analysed for soluble arsenic by the modified method of Gooch and Browning (*loc.cit.*), 500 cc. equivalent to 2·5 grms. of the arsenate being used in each determination. The alkali water used in the tests was the extract from a natural alkali incrustation containing 50 per cent Na_2SO_4, 18 per cent NaCl, 13 per cent Na_2CO_3, and 2 per cent $NaHCO_3$. The arsenic is reported as per cent of the original material.

It appears from the above results that both forms of the lead arsenate are more soluble in saline waters than in pure waters. Alkaline carbonate waters especially exert a solvent action on these arsenates, and the reaction is much more pronounced in the case of the acid arsenate. This is, perhaps, due to the fact that lead carbonate is extremely insoluble, and that a base with which arsenic forms a soluble salt is present. It is evident that waters containing considerable quantities of alkali carbonates should be avoided in mixing lead arsenate for spraying purposes, as their tendency is to render the arsenic soluble. Tests for lead in the alkaline solutions failed to show its presence therein.—*Journal of Industrial and Engineering Chemistry*, ii., No. 7.

Soluble Arsenic Pentoxide from Neutral and Acid Lead Arsenates.

Solution used.	Bean's ortho arsenate. Sol. As_2O_5. Per cent of moist arsenate.	Hemingway's acid arsenate. Sol. As_2O_5 Per cent of moist arsenate.
Distilled water..	0·073	0·108
Distilled water + CO_2 for two hours	0·125	—
0·23 per cent NaCl, 0·46 per cent $CaCl_2$	0·201	0·310
0·10 per cent Na_2SO_4	0·106	0·155
Alkali water, 40 grains to gal.	0·536	1·833

THE FRIEDEL AND CRAFTS REACTION WITH CHLORIDES OF UNSATURATED ACIDS.*

By E. P. KOHLER, G. L. HERITAGE, and M. C. BURNLEY.

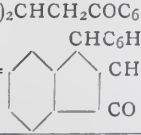
The following investigation was undertaken in connection with the preparation of an extensive series of $\alpha\beta$-unsaturated ketones for the purpose of comparison by physical measurements. Many of these ketones are very easily obtained by the Schmidt-Classen (*Ber.*, xiii., 2342) condensation of an aldehyde with a saturated ketone, but with aliphatic aldehydes, and with aromatic aldehydes in which the carbonyl group is in an aliphatic side-chain, the method generally gives aldols from which water is eliminated with difficulty, or else complex products not closely related to unsaturated ketones. We decided therefore to ascertain to what extent the Friedel and Crafts reaction can be used for preparing such ketones. The investigation led to the discovery of a number of facts of general interest in connection with the Friedel and Crafts reaction. These are published in this paper.

The literature on the subject under investigation is meagre. The reaction was first applied to unsaturated chlorides by Stockhausen and Gattermann in 1892 (*Ber.*, xxv., 3536). These investigators started with the chlorides of cinnamic and phenylpropiolic acids, and obtained an excellent yield of the expected unsaturated ketone when they used anisol or phenetol, but could isolate no solid products when they used aromatic hydrocarbons. They attributed this result to the difference in the reactivity of phenol ethers and hydrocarbons.

Many years later Moureu studied the reaction between the chloride of acrylic acid and benzene in the presence of aluminium chloride (*Ann. Chim. Phys.*, [7], ii., 198). He isolated a small quantity of a solid product that he assumed to be vinylphenyl ketone, but which was, in reality, α-hydrindone. It was shown a few years ago, that a satisfactory yield of unsaturated ketone can be obtained both with crotonyl chloride and benzene (*Am. Chem. Journ.*, xlii., 375), and with cinnamyl chloride and mesitylene (*Ibid.*, xxxviii., 510).

We have found that the reaction between cinnamyl chloride and benzene takes place almost as readily as that between the same chloride and phenol ethers, but the product is a mixture of two saturated ketones – diphenylpropiophenone and phenylhydrindone :—

I. $C_6H_5CH{:}CHCOCl + 2C_6H_6 = (C_6H_5)_2CHCH_2COC_6H_5 + HCl.$

II. $C_6H_5CH{:}CHCOCl + C_6H_6 =$  $+ HCl.$

* From the *American Chemical Journal*, xliv., No. 1.

A reaction between crotonyl chloride and benzene, similar to that represented by the first equation, was described in an earlier paper. It was there pointed out that such a result might be due either to the addition of hydrogen chloride to the unsaturated ketone first formed, and subsequent reaction with a second molecule of benzene, or to 1-4-addition of an organic aluminium compound to the same unsaturated ketone. We have not succeeded in getting any conclusive evidence in favour of either of these mechanisms.

The reaction expressed by the second equation represents a new indene synthesis which differs from that devised by Kipping in that a benzene nucleus introduced by means of the Friedel and Crafts reaction, and not one already present in the acid chloride, forms the foundation of the bicyclic system. The difference is illustrated by the following equations, which represent the synthesis of α-hydrindone :—

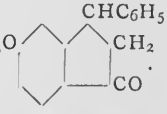
I. $C_6H_5CH_2CH_2COCl \rightarrow C_6H_4<^{CH_2}_{CO}>CH_2 + HCl$,

II. $CH_2{:}CHCOCl \rightarrow CH_2{:}CHCOC_6H_5 \rightarrow$
$\rightarrow C_6H_4<^{CH_2}_{CO}>CH_2$.

The difference in the results obtained when cinnamyl chlorlde is condensed with benzene and with anisol may be due, in part, to the greater reactivity of phenol ethers, as assumed by Stockhausen and Gattermann ; but this is certainly not the principal factor. With crotonyl chloride and benzene it is possible to conduct the reaction so as to get, at will, either saturated or unsaturated ketone. In concentrated solutions and at low temperatures the product is the unsaturated ketone, because under these conditions the aluminium chloride derivative of this ketone is so sparingly soluble that it separates quickly, and thus escapes further reaction. In more dilute solutions and at a higher temperature the aluminium chloride derivative remains in solution long enough to react with a second molecule of benzene, and this process takes place so readily that when only one equivalent of benzene is used nearly half of the acid chloride is left unchanged. The determining factor in this case is therefore the solubility of the aluminium chloride derivative of the unsaturated ketone.

The reactions with cinnamyl chloride cannot be controlled like those with crotonyl chloride because the double compound between the acid chloride and aluminium chloride is so slightly soluble that it is necessary to use higher temperatures and more dilute solutions. Phenol ethers give unsaturated ketones, nevertheless, because the alkoxyl groups hinder or prevent the secondary reactions that lead to saturated compounds. Thus indene synthesis does not take place because this would necessitate closure of the second ring in the meta position with reference to alkoxyl :—

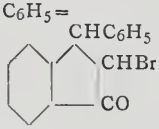
$C_6H_5CH{:}CHCOCl + C_6H_5OCH_3 =$
$= C_6H_5CH{:}CHCOC_6H_4OCH_3(p)$.

$C_6H_5CH{:}CHCOC_6H_4OCH_3(p) \rightarrow$ 

Our experiments show that the secondary reaction involving addition of a molecule of phenol ether to the unsaturated ketone first formed is likewise impossible—probably owing to the stability of the double compounds that alkoxy ketones, as well as phenol ethers, form with aluminium chloride. For similar reasons it is just as easy to get unsaturated ketones by using mesitylene as it is by using phenol ethers.

These results showed that the Friedel and Crafts reaction can be used in exceptional cases only for making αβ-unsaturated ketones. As these substances are easily made by removing bromine from αβ-dibrom ketones, we also made some experiments for the purpose of determining to what extent these can be made by condensing the chlorides of αβ-dibrom acids with aromatic hydrocarbons.

Collet (*Comptes Rendus*, cxxv., 306) added aluminium chloride to a solution of αβ-dibromhydrocinnamyl chloride in benzene, and obtained a solid, melting at 86°, which he assumed to be benzalacetophenone dibromide. We obtained the same product, but found that Collet had misinterpreted the reaction. The substance contains but one atom of bromine. As it gives *o*-benzoylbenzoic acid on oxidation, it must be an indene derivative formed according to the equation—

$C_6H_5CHBrCHBrCOCl + C_6H_5 =$  $+ HCl + HBr$.

Similar products were obtained when the same acid chloride was used with other aromatic compounds. The yield was poor in all cases because aluminium chloride attacks the acid chloride itself at the lowest temperature at which it is possible to carry out the reactions.

With chlorides of the corresponding dibrom aliphatic acids, however, the Friedel Crafts reaction gives an excellent yield of dibrom ketones.

Experimental Part.

Cinnamyl Chloride and Benzene.—In the first experiments equimolecular quantities of chloride and hydrocarbon were dissolved in carbon bisulphide and treated with aluminium chloride, but we found that the product always contained a large quantity of unchanged chloride. This was the case, also, when the acid chloride was first transformed into the Perrier double compound with aluminium chloride, and this treated with one molecule of benzene dissolved in carbon bisulphide. In all subsequent experiments the hydrocarbon was therefore used in excess. The reaction was studied under the following conditions :—

1. In carbon bisulphide cooled in a freezing mixture (− 20°). No perceptible reaction took place in the dark. In direct sunlight the aluminium chloride dissolved, then the Perrier double compound separated in small yellow crystals which re-dissolved very slowly with evolution of hydrochloric acid.

2. In carbon bisulphide at the ordinary temperature. The aluminium chloride dissolved with brisk evolution of hydrochloric acid, and the reaction was complete after the addition of slightly more than one molecule of aluminium chloride.

3. The double compound between cinnamyl chloride and aluminium chloride was made in carbon bisulphide, the solvent removed by decantation, and the crystalline solid covered with benzene. The reaction that started in the dark was completed in the sunlight.

The orange-coloured liquids obtained in these reactions were poured into iced acid, the organic products extracted with ether, and the extracts washed with sodium carbonate and dried. The yellow liquids left after removal of the solvents in no case contained benzolacetophenone, for while they reduced potassium permanganate they did not combine with bromine. After standing in an ice-chest for several days, the residue obtained by the first procedure partially solidified. The solid was purified by crystallisation from methyl alcohol, from which it separated in large colourless prisms, melting at 78°.

Analysis.

0·1217 grm. substance gave 0·3858 grm. CO_2 and 0·0657 grm. H_2O.

	Calculated for $C_{15}H_{12}O$.	Found.
C	86·6	86·4
H	5·8	5·9

As the substance has the composition and melting-point of a ketophenylhydrindene previously obtained by the action of aluminium chloride on ββ-diphenylpropionyl chloride, it was compared with a preparation made in this way, and thus identified as 3-keto-1-phenyl-2.3-dihydroindene.

A second product of the reaction was obtained by dissolving the residue from the indene derivative in petroleum ether, and cooling the solution in a freezing mixture. After purification this was easily recognised as $\beta\beta$-diphenylpropiophenone, which melts at 96°.

The filtrates from ketophenylhydrindene and diphenylpropiophenone contained a substance that decolorised a cold solution of permanganate in acetone, but no solid product could be isolated. The solvents were therefore removed, and the residual liquid heated under diminished pressure; it lost hydrochloric acid freely above 150°. and gave a distillate in which benzalacetophenone was recognised by transformation into its dibromide. This result indicated the presence of β 3-chlorphenylpropiophenone in the original product and in all subsequent experiments this substance was isolated by adding to the residues a crystal of a preparation made by direct addition of hydrogen chloride to benzalacetophenone.

All methods of procedure gave variable amounts of the same three products, ketophenylhydrindene, diphenylpropiophenone, and chlorphenylpropiophenone. The presence of a small quantity of the halogen compound is easily explained because it results from direct addition of hydrochloric acid to benzalacetophenone. A number of experiments were made for the purpose of discovering the mechanism by which the other products are formed, but the results are inconclusive. The total amount of these two products formed in any experiment could be estimated with considerable accuracy because they were the only indifferent substances left after the halogen ketone had been destroyed with permanganate. They always constituted 93 to 95 per cent of the entire product; but the relative amounts of the two varied within wide limits in experiments in which the conditions were intended to be as nearly as possible the same. Neither was obtained in more than insignificant quantities in all attempts at condensing benzalacetophenone or chlorphenylpropiophenone with benzene in the presence of aluminium chloride.

Cinnamyl Chloride and Brombenzene.—The reaction was carried out in carbon bisulphide at 0°. In one case ground aluminium chloride was added, in small quantities, to a solution containing cinnamyl chloride and excess of brombenzene, and in another excess of brombenzene was added gradually to a suspension of the double compound between cinnamyl chloride and aluminium chloride, but the result of both experiments was essentially the same. The solvent and the excess of brombenzene were removed by distillation with steam, and the residual brown paste dissolved in boiling absolute alcohol. This solution, on cooling, deposited a solid that, after a few re-crystallisations from alcohol, melted at 99—100°.

Analysis.

0·1708 grm. substance gave 0·3920 grm. CO_2 and 0·0590 grm. H_2O.

	Calculated for $C_{15}H_{11}OBr$.	Found.
C	62·71	62·58
H	3·83	3·84

The substance combined with bromine at −20°, and rapidly reduced potassium permanganate, being oxidised to benzoic and *p*-brombenzoic acids. The same substance was readily obtained by adding a small quantity of aqueous potassium hydroxide to an alcoholic solution of equimolecular quantities of benzaldehyde and *p*-bromacetophenone. It is therefore *benzal-p-bromacetophenone*, $C_6H_5CH:CHCOC_6H_4Br$. The unsaturated ketone is readily soluble in alcohol, ether, and acetone; sparingly in ligroin. It separates from all of these solvents in pale yellow friable plates that melt at 100—101°.

The reaction with aluminium chloride gave only a small quantity of benzal-*p*-bromacetophenone, the largest yield not exceeding 25 per cent of the possible quantity. The filtrates from this substance deposited a second product, which was purified by re-crystallisation from ligroin.

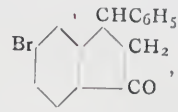
Analysis.

0·1332 grm. substance gave 0·3053 grm. CO_2 and 0·0463 grm. H_2O.

	Calculated for $C_{15}H_{11}OBr$.	Found.
C	62·75	62·5
H	3·83	3·9

The substance is isomeric with benzalbromacetophenone but neither reduces permanganate nor combines with bromine. It is therefore the corresponding indene derivative.

6-Brom-3-keto-1-phenyl-2,3-dihydroindene,—



is readily soluble in all common organic solvents. It separates from alcohol and from ether in prisms, from ligroin in large lustrous plates. It melts at 60—61°. The yield was 30 to 35 per cent of the possible quantity.

Cinnamyl Chloride and Phenol Ethers.—The experiments of Stockhausen and Gattermann with anisol and phenetol were repeated under different conditions, but no substance of the type of ketophenylhydrindene and diphenylpropiophenone could be detected in the products; excess of phenol ether does not affect the result in any way, and higher temperatures simply lead to decomposition products of the unsaturated ketone. A similar result was obtained with cinnamyl chloride and diphenyl ether. This reaction takes place very slowly, even in direct sunlight, but the yield of unsaturated ketone is excellent, because the aluminium chloride derivative is very sparingly soluble in carbon bisulphide.

Benzal-p-phenoxyacetophenone,—

$$C_6H_5CH:CHCOC_6H_4OC_6H_5,$$

is readily soluble in ether and acetone, moderately so in alcohol, sparingly in ligroin. It crystallises in pale yellow plates that melt at 85°.

Analysis.

0·1571 grm. substance gave 0·4794 grm. CO_2 and 0·0736 grm. H_2O.

	Calculated for $C_{21}H_{16}O_2$.	Found.
C	83·97	84·34
H	5·36	5·47

β-Diphenyl-p-phenoxypropiophenone,—

$$(C_6H_5)_2CHCH_2COC_6H_4OC_6H_5.$$

—The reaction between phenylmagnesium bromide and benzalphenoxyacetophenone is similar to that between the same reagent and benzalacetophenone; the sole product is a saturated ketone resulting from 1,4-addition. The substance was purified by re-crystallisation from acetone and alcohol, from which it separated in needles melting at 103°.

Analysis.

0·2107 grm. substance gave 0·6604 grm. CO_2 and 0·1137 grm. H_2O.

	Calculated for $C_{27}H_{22}O_2$.	Found.
C	85·71	85·48
H	5·82	5·99

The ketone is readily attacked by bromine, but the action of this reagent is not, as usual, confined to the hydrogen in the α-position. Thus, when one molecule of bromine was added to one of the ketone dissolved in warm chloroform, the solid that separated was found to be a mixture of mono- and dibrom substitution products. A partial separation of the mixture was accomplished by extraction with cold chloroform. The more soluble component, after repeated re-crystallisation from a mixture of chloroform and alcohol, separated in needles, melting at 163—165°.

Analysis.

1·1582 grm. substance gave 0·4072 grm. CO_2 and 0·0597 grm. H_2O.

	Calculated for $C_{27}H_{21}O_2Br$.	Found.
C	70·89	70·19
H	4·62	4·19

The bromine in this compound is in the aliphatic side-chain, because all of it can be removed by boiling with potassium hydroxide. The substance is therefore α brom-β 3-diphenyl-*p*-phenoxypropiophenone.

The residue left after extraction with cold chloroform was re-crystallised from boiling chloroform. It separated in minute needles melting at 211—212°.

Analysis.

0·1287 grm. substance gave 0·2845 grm. CO_2 and 0·0461 grm. H_2O.

	Calculated for $C_{27}H_{20}O_2Br_2$.	Found.
C	60·82	60·28
H	3·75	3·97

As only part of the bromine in this compound is eliminated by boiling with bases, the remainder must be located in a nucleus; it is probably in the *para* position of the phenoxyl group, $(C_6H_5)_2CHCHBrCOC_6H_4OC_6H_4Br$.

(To be continued).

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,*

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, &c.

By PERCY H. WALKER.

(Continued from p. 44).

Paint Materials (*continued*).

Benzine and Light Petroleum Oils.

The term benzine is used for a number of light petroleum oils. In the painting trade it generally refers to a product of about 62° Baumé (0·7292 sp. gr.). The petroleum benzine of the U.S. Pharmacopœia is a lighter oil, being a light gasoline.

1. *Specific Gravity.*—Determine with a spindle, pyknometer, or plummet at 15·5° C. The determination can be made at room temperature and corrected to 15·5° C.

2. *Sulphur (Sodium Nitroprusside Test).*—To 100 cc. of the sample in a flask add about 1 grm. of bright metallic sodium, connect with a reflux condenser, and boil for one hour. Cool, add water drop by drop until the metal is dissolved, separate the aqueous liquid, and test with a drop of sodium nitroprusside solution. A fine violet-blue coloration indicates sulphur.

3. *Sulphur Compounds and Pyrogenous Products (U.S.P. Test).*—To 100 cc. of the sample add 25 cc. of a solution of 10 per cent anhydrous ammonia in 95 per cent alcohol (spirit of ammonia U.S.P.), add 1 cc. of silver nitrate solution. Boil gently for five minutes. A brown coloration indicates sulphur compounds or pyrogenous products.

4. *Residue on Evaporation.*—Place 25 cc. in a 100 cc. platinum dish, heat on steam-bath for thirty minutes, and weigh residue. No residue should be left by this test.

5. *Fractional Distillation.*—Light petroleum oils are usually tested only for specific gravity; but as light and heavy distillates may be mixed, the specifications would be improved by requiring that a certain fraction should distil between specified temperatures. To make this determination distil 100 cc. in a round-bottom flask 6·5 cm. in diameter; the neck should be 1·6 cm. in diameter, and 15 cm. long, with a side-tube set in the middle of the neck at an angle of 75°. The surface of the liquid should be 9 cm. below the side-tube, and the bulb of the thermometer just below the side-tube.

6. *Benzol.*—Mix the sample with 8 volumes of strong sulphuric acid and 2 volumes of nitric acid; heat gently for ten minutes, allow to cool, and note odour. The odour of nitrobenzol indicates benzol.

7. *Colour and Odour.*—Note colour of sample and odour both in bulk and after rubbing on hands.

Dry Shellac.

1. *Detection of Rosin (Liebermann-Storch Test).*—To 1 grm. of the sample add 15 cc. of acetic anhydride, heat gently until solution is complete, cool, draw off the acetic anhydride, and add a drop of sulphuric acid 1·53 specific gravity. A fugitive violet colour indicates rosin.

2. *Determination of Rosin (Langmuir's Method) (Journ. Soc. Chem. Ind.*, 1905, xxiv., 12—17).—To 0·200 grm. of ground shellac, in a 250 cc. dry bottle of clear glass with a well fitting ground glass stopper, add 20 cc. glacial acetic acid, and warm gently until the shellac is dissolved (a little shellac wax will remain undissolved, and at least half-an-hour should be allowed, for the shellac itself is difficultly soluble). Then add 10 cc. of chloroform and cool the solution down to 21° to 24° C. Add 20 cc. of Wijs's iodine monochloride solution, shake, and keep in the dark at a temperature between 21° and 24° C. for one hour, add 10 cc. of potassium iodide solution, and titrate immediately with thiosulphate—25 cc. may be run in at once, and the remainder gradually with vigorous shaking, adding starch solution just before the end. The end-point is sharp; any colour returning after half-a-minute or so may be disregarded. If less than 25 cc. thiosulphate is required, reject result and repeat determination, using a smaller quantity of shellac.

The Wijs solution may be made either by dissolving iodine monochloride in glacial acetic acid or by dissolving iodine in glacial acetic acid and passing in dry chlorine until the halogen content (figured as iodine) has nearly doubled; there may be a very slight excess of iodine, but there must be no excess of chlorine above the theory for iodine chloride. The halogen content figured as iodine should be about 26 grms. per 1000 cc. The glacial acetic acid used must be free from reducing substances and have a melting-point between 14·7° and 15° C. The thiosulphate solution should be a decinormal sodium thiosulphate solution. The potassium iodide solution is 10 per cent. Blanks must be run each time and the iodine number calculated from the difference between the titration result on the blank on the sample. Calculate the per cent of rosin, using the formula: $y = 100\frac{A-M}{N-M}$, where y = per cent rosin, M = iodine number of shellac, N = iodine number of rosin, and A = iodine number determined.

In calculating the percentage of rosin, assume the iodine number for pure rosin to be 228, that for pure unbleached shellac to be 18, and for pure bleached shellac 10. These figures will tend to give somewhat low results on rosin percentage, but should be used, as it is then safe to say that there is *at least* as much rosin present as is found by analysis.

3. *Alcohol Insoluble.*—Add to 1 grm. of shellac 60 cc. of 95 per cent alcohol, heat to boiling, and filter on a Gooch crucible; wash with about 60 cc. of boiling 95 per cent alcohol, dry at 100° C., and weigh.

4. *Loss on Drying—Water.*—Heat 1 grm. for two hours in a water oven at 100° C. Loss in weight is calculated as water.

5. *Ash.*—Determine ash on 1 grm., heating only to dull redness.

Shellac in Alcohol.

1. *Total Solids and Ash.*—Evaporate 1 grm. of the varnish in a porcelain dish on the water-bath and dry to constant weight in steam oven (about five hours). Ash residue as in dry shellac.

* *Bulletin* No. 109, Revised, U.S. Department of Agriculture Bureau of Chemistry.

2. *Examination of Solvent.*—Note the odour of the varnish, as little can be learned from the odour of the distillate. Distil 100 grms. of the varnish until incipient decomposition begins; re-distil the distillate, noting the boiling-point, and determine the specific gravity of the distillate. By this means it is usually an easy matter to determine whether the varnish is made with wood alcohol, grain alcohol, or denatured alcohol. Dilute a portion with three times its volume of water; if benzine is present it will separate.

3. *Test for Rosin.*—Do not use the residue from the total solids determination, but carefully weigh in a capsule a quantity of varnish sufficient to yield 0·2 grm. of solid material, evaporate to a paste, and treat the residue as described under "dry shellac," paragraphs 1 and 2.

Damar Varnish.

Damar varnish, which should be a solution of damar gum in spirits of turpentine, is examined by the methods for oil varnishes (see below). The percentage and nature of the volatile oil, specific gravity, and flash-point are important tests. It should yield little ash, which should contain no lead or manganese. When flowed on glass it should set to touch in a very short time (less than thirty minutes) and mixed with zinc white should yield a good white enamel surface when applied to wood.

In testing for rosin by the Liebermann-Storch test (see below), the light claret colour characteristic of damar should not be mistaken for the violet colour characteristic of rosin. The Hirschsohn test for rosin, which is less delicate than the Liebermann-Storch method, is as follows:—

Digest about 1 grm. of the dried resin with approximately 20 cc. of ammonium hydroxide for twenty minutes, filter and acidify with acetic acid. With pure damar the liquid remains clear, but if rosin is present a precipitate forms, and when the proportion of rosin is large the entire acid liquid may become gelatinous. The acid number of damar is lower than that of rosin and higher than that of the hard varnish gums. An oil varnish made of hard gums will generally have an acid number of less than 12. A damar varnish will have an acid number between 15 and 20, a higher number generally indicating the presence of rosin.

Oil Varnish.

The methods of analysis for varnish are far from satisfactory. A number of methods for determining the amount of gums in varnish have been proposed, but none of them are reliable. This determination, therefore, is not made, but the combined percentage of oil and gums is reported.

1. *Appearance and Odour.*—Transfer the sample if it is in a metal container to a glass-stoppered cylinder or bottle and note its appearance, colour, transparency, body, and whether any sediment is deposited. The presence of light petroleum oil or wood turpentine may often be detected by noting the odour of the sample. After making these observations, the sample should be thoroughly mixed before making the remaining tests.

2. *Specific Gravity.*—Determine with a pyknometer, plummet, or hydrometer at 15·5° C.

3. *Flash-point.*—Determine as in spirits of turpentine; but begin testing at 25° C. and stir the varnish while heating. A low flash-point indicates light petroleum oil.

4. *Viscosity.*—The determination of viscosity is seldom necessary; but, if desired, make the determination by the Engler-Ubbelohde method at 20° C.

5. *Volatile Oils.*—Weigh 100 grms. of the varnish into a 500 cc. flask, connect with a spray trap and a vertical condenser, and pass through it a current of steam, first heating the flask in an oil-bath at 100° C.; with the steam still passing through, raise the temperature of the bath to 130° C. Catch the distillate in a small weighed separatory funnel; continue distillation until 300 cc. of water has been condensed. Portions of this water may be drawn from the cock of the separatory funnel from time to time, but care must be taken not to draw out any of the volatile oil. Let the distillate stand until it separates into two layers, then draw off the water and weigh light oils. Filter the light oils through dry paper, and examine as directed under spirits of turpentine (see above). A slight error is caused by the solubility of turpentine in water; this amounts to about 0·3 to 0·4 cc. for each 100 cc. of water.

When sufficient varnish is available, it is well to take another portion and distil, without steam or spray trap, placing the weighed flask in an oil-bath. Note the temperature of the bath at which distillation begins, and continue distillation at a temperature of 185° C. in the oil-bath, finally raising the temperature to 200° C. This method generally tends to give lower results on volatile oils than the steam distillation method; but the distillate can be tested for water-soluble volatile liquids, which would be lost by the steam distillation.

6. *Fixed Oil and Gums.*—The percentage of fixed oil and gums is obtained by subtracting the percentage of volatile oils from 100. A check upon this determination is obtained by weighing the residue from the dry distillation.

7. *Acid Number.*—Determine the acid number in the usual way, using 10 grms. of varnish.

8. *Rosin.*—After getting the acid number, decant the alcohol, evaporate, and apply the Liebermann-Storch test for rosin (see above).

9. *Ash.*—Determine the ash in 10 grms., using a quartz or porcelain dish and carrying out the determinations at a low heat, best in the muffle. Determine the reaction of the ash to litmus-paper and make a qualitative analysis. It is frequently well to make a quantitative determination of lime, a large amount of which indicates rosin. It is sometimes advisable to determine the percentage of lead and manganese. Some lead will, however, be lost in the ashing, and if a correct lead determination is required, follow the method described for mixed paint vehicle (see *prox.*).

10. *Miscellaneous.*—It is not possible from such an examination as has just been described to decide on the value of a varnish for any particular purpose, though valuable information as to the materials used in its manufacture may be obtained. An examination of the varnish film should, therefore, always be made. The films are best made by flowing the varnish on carefully cleaned plates of glass, and allowing to dry at room temperature in a vertical position. Observe the time of setting and the nature of the film after twenty-four hours, noting the transparency, hardness, elasticity, tendency to dust by scratching, &c. After thorough drying, immerse the plate in water over night, dry, and note appearance. The working quality of a varnish must be determined by application on wood, and it is best to make this test on well seasoned and perfectly smooth white pine. Apply a thin coat of the varnish to wood and allow to dry, sandpaper down smooth, and then apply the coat to be tested. Observe how the varnish works under the brush, character of coat, &c. This panel, after drying, may be used for further testing as to whether the varnish will stand rubbing, &c.

Japan Dryer.

The analysis of Japan dryer is conducted in the same way as that of varnish. The following specifications for Japan dryer for the Philadelphia and Reading Railroad are given in an article by Job on "Practical Testing and Valuation of Japan" (*Chemical Engineer*, 1906, iv., 198):—

The material desired consists of a pure turpentine hardener and oil drier, conforming to the following:—

1st. When equal parts by weight of the Japan and of pure turpentine are thoroughly mixed and poured over a slab of glass, which is then placed nearly vertical at a temperature of 100° F., with a free access of air but not exposed to draught, the coating shall be hard and dry, neither brittle nor sticky, in not exceeding twelve minutes.

2nd. When thoroughly mixed with pure raw linseed oil at the ordinary temperature in proportions of 5 per cent by weight of Japan to 95 per cent by weight of raw linseed

oil, no curdling shall result, nor any marked separation or settling on standing.

3rd. When the above mixture is flowed over a slab of glass, which is then placed nearly vertical at a temperature of 100° F., with free access to air but not exposed to draught, the coating shall dry throughout, neither brittle nor sticky, in not exceeding two hours.

4th. When 5 cc. of the Japan are poured into 95 cc. of pure turpentine at the ordinary temperature, and thoroughly shaken, a clear solution shall result, without residue, on standing one hour.

5th. After evaporation of the turpentine, the solid residue must be hard and tough, and must not "dust" when scratched with a knife.

6th. Benzine or mineral oil of any kind will not be permitted.

This, with the following specification of the U.S. Navy Department, will furnish a very good basis for an examination of Japan drier: –

1. Japan dryer must not flash below 105° F. (open tester); must be of the best quality and made from pure kauri gum, pure linseed oil, pure spirits of turpentine, and lead manganese driers, and be free from adulterants and all other foreign materials; must set to touch in from one-fourth to one hour, dry elastic in from eighteen to twenty-one hours at a temperature of 70° F., and must not rub up or powder under friction by the finger. When mixed with pure raw linseed oil in the proportion of 8 parts of oil to 1 part of drier, must remain clear for two hours and set to touch in from six to seven hours at a temperature of 70° F.

(To be continued).

SCIENCE SECTION, JAPAN-BRITISH EXHIBITION.

An inspection of the British Science collection was arranged on Friday, July 22nd, under the direction of Sir Alexander Pedler and Dr. Divers. The exhibits are much more numerous and complete than would appear to the casual observer, and comprise Oceanography, Astronomy, Anthropology, Meteorology, Physics, Geography, Biology, Chemistry, Palæontology, Geology, Mathematics, and Agriculture. A representative for each section was present, who pointed out the leading features of the various exhibits. Want of space prevents us from doing more than draw attention to some of the more important, but the whole Section will well repay careful study.

Oceanography. — Since the expedition of H.M.S. *Challenger* in 1870 to the present date much has been recorded of the depth and temperature of the ocean, and a very complete series of charts are shown. The greatest depth is a little over 5000 fathoms, or between 30,000 and 32,000 feet; the temperature decreases from the surface to the bottom, where it is little if anything above the freezing-point of fresh water; many forms of sounding and temperature recording apparatus are shown.

The Royal Observatory, Greenwich, contributes a very interesting series of photographs and transparencies. Amongst these will be noticed a selection from the valuable series of 162 photographs of Comet Morehouse, taken in 1908, showing the rapid and continuous changes in the tail of the comet; a transparency from the negative from which Mr. Melotte was able to make his remarkable discovery of the eighth satellite of Jupiter; some fine photographs of sun-spots, and of the Corona taken at various eclipse expeditions.

There are also photographs of the sixth, seventh, eighth satellites of Jupiter, the ninth satellite of Saturn, and the satellite of Neptune, all made at the Royal Observatory.

A very fine collection of Astrolabes, Quadrants, and Sun-dials belonging to Mr. Lewis Evans is shown. In this collection is a Norman dial of the third or fourth century, and a dial formerly belonging to Cardinal Wolsey.

The Anthropological exhibit organised by Mr. John Gray, B.Sc., contains two remarkable prehistoric skulls, the Gibraltar skull and the Galley Hill skull; the former of these is said to be 200,000 years old, and the Galley Hill skull, the only undoubted palæolithic skull found in England, is thought to be at least 100,000 years old.

Mr. J. Gray also exhibited a series of maps to represent some of the results of his Pigmentation survey of the school children of Scotland.

The instruments exhibited include the latest designs for making all the ordinary physical measurements, such as weighing-machines, callipers, height meters, pigmentation meters. There are also several interesting appliances for making mental measurements, such as Dr. McDougall's spot pattern apparatus, Dr. Spearman's mental tests, Gray's perseveration apparatus.

In the Mechanics Section are pendulums, tapes, and other apparatus made in C. Guilleaume's nickel-steel alloy known as invar, which has an exceedingly low coefficient of expansion, and the Cambridge Scientific Instrument Co. show a new device for calibrating spirit levels, as well as Mr. Duddell's oil-bath oscillograph and Prof. Callendar's temperature recording apparatus.

In the Geographical Society's exhibit there is a very interesting series of photographs of the original maps made by early African explorers, including some by David Livingstone and Sir H. M. Stanley.

Perhaps the most interesting exhibit is the small collection of old instruments used by well-known early explorers, including the sextant with which Dr. Livingstone took his observations in Central Africa, and the compass with which he navigated his boat down the Zambezi in 1856, when the course of the river was followed for the first time.

Biology.—This exhibit, which was organised by Prof. E. W. McBride, LL.D., F.R.S., of the Imperial College of Science and Technology, with the assistance of H. Hammond-Smith, M.D., illustrates some of the researches which have engaged the attention of British zoologists for the last ten years.

Among the most interesting items in this Section is an example of parental care in fishes; in one instance the eggs are carried and hatched in the mouth, while in another they are carried in a pouch on the abdomen like the kangaroo.

Chemistry is but poorly represented, but some valuable original researches are illustrated.

A complete exhibit of the work of the late Dr. Ludwig Mond illustrates the technically important process for purifying nickel from cobalt, &c., by means of nickel carbonyl. In addition to nickel it has been found possible to separate molybdenum as well as cobalt, iron, rhodium, and all the members of the VIIIth group. A complete set of the metallic carbonyls is shown, these substances constituting a new departure in the chemistry of the metals.

Messrs. Hopkins and Williams display fine specimens of radio-active minerals and salts, a collection of rare earths employed in the incandescent mantle industry, and a series of the rarer cinchona alkaloids and their derivatives.

The University of Leeds is represented by the work of three of its professors of chemistry. Dr. Cohen sends specimens illustrating the relation of optical activity and chemical structure, whilst Professors A. G. Perkin and A. G. Green show specimens illustrating their researches on the natural and artificial colouring matters respectively.

Interesting collections are lent by the Wellcome Chemical and Physiological Research Laboratories, and a great many specimens, models, and photographs are shown connected with the investigations upon tripanosomiasis (sleeping sickness) that are being carried out at that institution; the former of these institutions showing a comprehensive exhibit of the important researches on plants of reputed medicinal value carried out by Dr. F. B. Power and his collaborators.

A new method of detecting prussic acid in animal and vegetable tissues is demonstrated by Professor A. D. Waller.

The substances obtained in the synthesis of optically active silicon compounds are shown by their discoverer, Professor Kipping, whilst the synthesis of camphor and menthol is illustrated by specimens sent by Dr. R. H. Pickard. The oxidation of organic acids in the presence of ferrous sulphate is an important reaction leading to the valuable products lent by Dr. Fenton.

Professor Crossley contributes a unique set of the nitration products of α-xylene, one of the constituents of coal-tar naphtha, together with an interesting collection illustrating the important problem of the utilisation of atmospheric nitrogon.

Dr. F. M. Perkin exhibits a series of chemical products prepared by electrolytic methods and also lends the apparatus designed by the late Sir William Perkin for the purpose of magnetic rotation.

Dr. G. T. Morgan, Miss Micklethwaite, and Mr. A. Clayton contribute several interesting exhibits bearing on the connection between colour and chemical constitution, and the first of these exhibutors also shows, in conjunction with Dr. Martindale, a set of compounds of therapeutic interest.

Professor Sudborough's preparations also bear on the relationship of colour and constitution, and Professor Senier sends a set of phototropic compounds, the colours of which undergo a reversible change when the substances are alternately exposed to light and then placed in the dark.

The erosion of the bronze propellers of high speed ships is illustrated by Dr. Silberrad, and Dr. Beilby furnishes evidence of molecular mobility in solids.

The volcanic regions of Japan furnish selenium and tellurium, the rare analogues of the common element sulphur. Fine specimens of these elementary forms of matter are exhibited by Professor Divers, the acting Chairman of the Science Section.

In the Mineralogical Section the Natural History Museum has contributed a large collection of minerals from the British Isles. A very beautiful series of photographs of polarisation figures in colours by the autochrome process is shown, and a case of specimens of artificial gems contain some very fine examples of rubies, colourless, yellow, and green sapphires.

Geology.—The most extensive exhibit in the Geological Section is that made by Prof. E. J. Garwood, of University College, London. Here are shown not only his ingenious apparatus for sounding lakes, but a geological model of the lake of Val Piora, near Airolo, with bathymetrical charts, photographic views, and specimens of the local rocks. Another part of Prof. Garwood's exhibit is a large series of specimens illustrating the stratigraphical sequence of rocks and fossils in the carboniferous limestone of the North of England, beautiful sections of zonal fossils so cut that the structure of the corals is finely displayed by transmitted light.

A beautiful model of the central part of the Isle of Skye is exhibited by Mr. Russell F. Gwinnell. By its geological colouring it clearly shows the relation of the scenic features of the country to the character of the rocks, which are here mostly of igneous orgin.

A large collection of photographs of volcanoes is exhibited by Dr. Tempest Anderson, of York. These were taken by him during a recent journey to the Pacific Islands, and include some remarkable photographs of the volcano of Matavanu, which was formed in 1905 in Savii, one of the German Samoan Islands. There are also photographs bearing on volcanic phenomena from Kilauea in Hawaii, and from New Zealand, whilst others by the same authority are placed in the Photographic Section.

University of Sheffield.—The Council have appointed Mr. A. E. Findley, B.Sc. (Birmingham), F.C.S., to the newly instituted post of Lecturer of Applied Chemistry in the University. Mr. Findley is at present Assistant Lecturer in Chemistry at the Bradford Technical College.

CORRESPONDENCE.

THE INVENTOR OF THE BLACK-ASH FURNACE.

To the Editor of the Chemical News.

Sir,—Owing to the kindness of Mrs. Black, of Harrow, grandniece by marriage of Dr. Joseph Black, I have been permitted to examine the correspondence of that celebrated chemist, and I have unearthed a bit of history of considerable interest.

The account of the invention of a method of making soda and sodium carbonate is given in Wurtz's Dictionary, edition 1876, p. 1556, in the following words :—

"En 1789, De La Métherie proposa de calciner le sulfate de soude avec du charbon, ésperant que la réaction s'accomplirait de manière à produire du carbonate de soude comme residu et un dégagement d'acide sulfureux. En réalité, il n'obtint que du sulfure de sodium, ou, suivant les circonstances (influence de l'acide carbonique et de la vapeur d'eau), un mélange de sulfure de sodium avec plus ou moins de carbonate de soude. Le procédé n'était donc point pratique, mais il mit un autre chercheur sur la véritable voie. Cet inventeur était Leblanc (né en 1740 á Issoudun, officier de santé, chirurgien du duc d'Orleans, Philippe-Egalité), qui, depuis 1787, s'occupait également de la solution du problème, et qui, en associant du calcaire au mélange de sulfate de soude et de charbon, le resolut, en effet, de la manière la plus satisfaisante.

"La réalité de le découverte de Lablanc ayant été constaté par d'Arcet et par son préparateur Dizé, le Duc d'Orléans consentit à verser un capital de 200,000 francs pour l'exploitation du procédé. Leblanc, associé avec Dizé et Shée (un homme d'affaires du duc), construisit la première fabrique de soude artificielle à Sainte-Denis et obtint, le 23 Septembre, 1791, sur le rapport de d'Arcet, Desmarets et de Servières un brevet d'invention de quinze années."

In 1782, Dr. Joseph Black received from Mr. Geo. Golder the following letter :—

Linen Hall, Edinburgh,
March 19, 1782

"Dear Sir,—I beg leave to send you herewith some samples of ashes manufactured by Messrs. Collison and Co., of London, which I beg the favour you will examine and give me your opinion of them.

"You have herewith copies of some letters on the subject; Mr. Sandeman, of Lanark, and others have seen and approved of them so far as they can judge without trial.—I am, respectfully, Sir, your most obedient servant,

Geo. Golder.

"Dr. Joseph Black, Physician, Nicolson's Street."

The accompanying paper was enclosed by Mr. Golder :—

"*Copy of Collison's Specification for making Mineral and Vegetable Alkali.*

"Now know ye, that in compliance with the said proviso, I, the said John Collison Do hereby declare that the nature of my said invention of a new art of producing or making vegetable or mineral alkali, and the manner in which the same is to be performed, is described and ascertained in the manner following, that is to say, as to for touching and concerning Mineral Alkali.

"I take Glauber's Salt, or any substance or liquor containing Glauber's salt, or I take rock-salt, sea-salt, or common salt, and any substance or liquor containing vitriolic acid, and mix these, so that the weight of the salt shall be nearly twice the weight of the concentrated vitriolic acid, which I heat together in an open fire, reverberatory furnace, iron pot, or other utsensil, together with from a quarter to half its weight of some, or one, or more of the following substances:—Videlicet, mortar, sopers' ashes, clay, gypsum, loam, calcareous, or other earth, and

and the same quantity, more or less, according to their different qualities, of horns, hoofs, hair, leather, scraps, pitch, tar, small vegetables, breeze, charcoal, pit-coal, or any other substances containing, or supposed to contain, an inflammable principle or phlogiston, or some, or one, or more of them; which, when properly heated, melted, or fluxed, produce a mineral alkali. And as for touching and concerning the vegetable alkali, I pursue the same process as above, except that I take Sal Polychrest, vitriolated tartar, or any substance or liquor containing vegetable alkali, instead of the salts and mixtures above mentioned."

Then follows a report by Black in draft:—

"Dear Sir,—I have examined the ash prepared by Collison and Co., and find it to be very strong and powerfull. It contains more alkali than the best Alicant Barilla in the proportion of 68 to 44, and more than the best Kelp in the proportion of 68 to 10; and the alkali which it contains is in a more active state than that of Barilla, insomuch that it would be dangerous in bleaching to use more than one hundred wt. of this ash in place of two or somewhat more of the best Barilla. It is an excellent ash for the Soap-boilers. It will take a quantity of tallow proportional to the alkali which it contains; that is, one-half more than the best Barilla; and there is no need to use lime in drawing the leys from it, as it is already in a caustic state.

"I made my essays on the black or grey ash; the bits of white ash appeared much weaker, but too little of it for an essay."

After this, there appears little doubt who invented the black-ash furnace.—I am, &c.,

William Ramsay.

NOTICES OF BOOKS.

Fertilisers and Feeding Stuffs. By Bernard Dyer, D.Sc. Sixth Edition, Revised. London: Crosby, Lockwood and Son. 1910.

The repeal of the original Fertilisers and Feeding Stuffs Act has necessitated the preparation of a new edition of this useful little book in order that the new Act may be included in it. In the sixth edition, which as far as the text goes is very little altered from the fifth, the Act of 1906 is reproduced in full with notes on its salient features by A. J. David, B.A., LL.M. The attention of the farmer is directed to the points in the new Act which it is to his advantage to know, and decisions upon the Act up to the present date are included.

The Compendium of Medicine and Pharmacy. By C. J. S. Thompson. Third Edition. London: John Bale, Sons, and Danielsson, Ltd.

This compendium is a handy book of reference for the medical practitioner, and will provide him with much useful information to which he can refer with ease and rapidity. It contains lists of new and unofficial remedies, with notes on their properties and doses, an index of diseases and their remedies, and some extracts from foreign pharmacopœias as well as from the British Pharmacopœia. In addition some methods of analysis which are used in the examination of drugs are described, and many conversion tables for weights and measures are given.

Two Academic Addresses. By Prof. Senier. Second Edition. Dublin: Edward Ponsonby. 1910.

These two addresses were the opening lectures of the sessions commencing in 1897 and 1901 respectively, and were delivered before the Students' Literary and Debating Society, Queen's College, Galway. The first describes a visit to Giessen, and gives a short biographical account of Liebig, explaining how he overcame his early difficulties and won the notice of the foremost chemists of his day, afterwards to surpass them all in the brilliancy of his researches and the value of his contributions to the science. The extraordinary influence of the great teacher upon his pupils is emphasised, and the lecture should prove inspiriting and stimulating to the young student of chemistry. The second address gives an account of the early history of Bonn on the Rhine, of the foundation of its University, and the latter's gift to England of one of its most distinguished members, Prof. Hofmann. This lecture suggests subjects for serious reflection connected with the advance of scientific education in this country, upon which question Prof. Senier entertains strong views.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cl., No. 21, May 23, 1910.

Action of Ortho- and Para-Anisyl Magnesium Bromides on Anthraquinone and β-Methylanthraquinone.—A. Haller and A. Comtesse.—The magnesium compounds of ortho- and parabromanisol give with anthraquinone and β-methylanthraquinone diols analogous to those formed by the action of phenyl magnesium bromide on these quinones. These diols are white crystalline substances, soluble in organic solvents, and giving characteristic colorations with concentrated sulphuric acid. Their acetic acid solution decomposes potassium iodide, setting iodine free and forming an anthracene derivative. They are very easily acetylated and etherified, and can be reduced without difficulty to γγ-disubstituted anthracenes, which are more or less yellow in colour and dissolve in organic solvents with the production of remarkable fluorescences.

Composition of Atmosphere after the Passage of Halley's Comet.—Georges Claude.—By determining the density of the uncondensable gaseous residues (mixtures of nitrogen, neon, helium, and hydrogen) in the atmosphere on the 17th, 19th, 20th, and 23rd of May, the author found that the composition of the atmosphere did not vary, at any rate, as far as the inert gases are concerned.

Solubility of Silver Sulphate in Alkaline Sulphates.—M. Barre.—The solubility of silver sulphate in potassium and ammonium sulphates increases regularly with the concentration of the alkaline salt; the curves obtained at different temperatures, taking as abscissæ the alkaline sulphate and as ordinate the silver sulphate in the solution, are straight lines for potassium sulphate and very nearly straight lines for ammonium sulphate. With sodium sulphate very different results are obtained. Below 33°, *i.e.*, as long as the sodium sulphate is hydrated, the solubility of silver sulphate increases with the concentration of the sodium sulphate. Above 33° the curves show a maximum but no angular point, and mixed crystals are formed. In solutions containing less than 40 per cent of sodium sulphate the solubility of the mixed crystals increases as the temperature rises, while with a higher concentration it decreases. When the concentration is 40 per cent the solubility is independent of the temperature. This peculiarity is due to the difference of sign of the heat of solution of silver sulphate and sodium sulphate.

Chemical Effects of High Pressures.—E. Briner and A. Wroczynski.—Nitrogen monoxide is much more stable at high pressures than nitric oxide, and a high temperature seems absolutely indispensable in order to decompose its molecule. No chemical action occurs when mixtures of

nitrogen and hydrogen are subjected to pressures up to 900 atmospheres. Carbon monoxide is decomposed into carbon dioxide and carbon at a pressure of 400 atmospheres.

Chemical Actions of Ultra-violet Rays on Gases.—Daniel Berthelot and Henri Gaudechon.—In presence of oxygen the ultra-violet rays bring about the complete combustion of cyanogen. The ultra-violet rays set free hydrogen from ammonia, and in presence of oxygen this is then oxidised to water, although free hydrogen and oxygen do not unite when subjected to the rays. They cause the synthesis of formic acid from acetylene and oxygen, and also from ethylene and oxygen.

Action of Ozone on Carbon Monoxide.—P. Clausmann.—Carbon monoxide is transformed directly into the dioxide by the action of ozone. Light accelerates the reaction, but is not absolutely essential. A trace of moisture also increases the yield of carbon dioxide.

Dehydrodicarvacrol.—H. Cousin and H. Hérissey.—Dehydrodicarvacrol can be prepared by allowing a solution of carvacrol to stand with ferric chloride for ten days, treating the precipitate obtained with a weak alkali, filtering and adding acetic acid solution, which precipitates the dehydrodicarvacrol. From the substance the authors have prepared the dimethyl, diacetyl, and dibenzoyl derivatives.

Ketones derived from Benzoic Acid and Phenylacetic Acid.—J. B. Senderens.—By the catalytic action of thoria the author has prepared pure ketones from a mixture of benzoic acid and a fatty acid, from phenyl acetic acid alone, and from a mixture of phenyl acetic acid with a fatty acid. All these ketones have a pleasant aromatic odour; they are soluble in water and very soluble in alcohol.

Determination of Origin of Naphtha and its Derivatives.—N. Cherchefsky.—The author has drawn up a table giving the following data for naphthas of various origins for the distillate obtained by fractionating the product under examination:—Density, boiling-point, index of refraction, index of solubility, critical temperature of solution, temperature at which turbidity appears, iodine index. By comparing the results obtained with a given specimen with the tabulated results not only can the origin of the naphtha or its derivative be determined, but also the approximate composition of commercial samples can be ascertained.

Condensation of Oxalic Ether with Tricarballylic Ether.—H. Gault.—Oxalic ether in presence of dry sodium ethylate combines molecule for molecule with tricarballylic ether, giving a mixture of monoxaltricarballylic ether and diketopentamethylene tricarbonic ether (cyclopentanedione tricarbonic ether). The latter is easily saponified, yielding either ketopentanedione dicarbonic acid ether, if the saponification is stopped as soon as the original product is completely dissolved, or if the action is prolonged cyclopentane dione monocarbonic acid is obtained.

New Synthesis of Natural and Racemic Erithrites.—H. Pariselle.—Epibromhydrine when heated with powdered potash yields 1.2-oxy-3.4-butene, which when shaken with water containing a few drops of sulphuric acid takes up water and gives erythrol. By the action of barium permanganate on erythrol natural erythrite is obtained. From the mother-liquor of the crystals racemic erythrite can be isolated.

No. 22, May 30, 1910.

Action of Heat on Carbon Monoxide.—Armand Gautier.—The author has found that, even at a white heat in absence of organic matter or a metal, carbon monoxide is not dissociated, giving carbon according to Deville's equation, $2CO = C + CO_2$. He believes that the presence of carbon dioxide and methane in volcanic gases is to be ascribed to the action of traces of hydrogen on the monoxide:—$2CO + H_4 = CO_2 + CH_4$.

Quantitative Measurements of Radium Emanation.—W. Duane and A. Laborde.—In 1905 Duane studied the laws of the ionisation produced in air by the radiations of radium emanation at atmospheric pressure and 15°. The saturation current depends upon the surface and volume of the condenser, and the equation giving it contains two constants which the authors have now determined by means of experiments carried out with solutions which have been used as standards in Mdme. Curie's laboratory.

Electrification of the Air by the Flame of Carbon Monoxide and Radium Rays.—Maurice de Broglie.—When the mobilities of the ions produced by the flame of carbon monoxide and by radium rays are compared by the method of gaseous currents, it is found that the values obtained for the mobilities are very close, and that they are probably identical.

Zinc Oxychlorides.—M. Driot.—The study of the solubility of the oxychlorides of zinc in solutions of the chloride of different concentrations at the ordinary temperature shows that two oxychlorides exist, their formulæ being $ZnCl_2.4ZnO.6H_2O$ and $ZnCl_2.ZnO.1{\cdot}5H_2O$. The former is a white amorphous substance while the latter forms microscopic crystals. The constitution of these oxychlorides does not vary with the temperature. There is no evidence of the existence of the eight other oxychlorides which have been described.

Rotatory Power of Pinene Chlorhydrate.—Gustav Vavon.—A solid chlorhydrate of pinene can be prepared by treating the different fractions obtained between 155° and 165° in the distillation of essence of terebenthene with dry hydrochloric acid gas at 30°, and the rotatory power of this chlorhydrate shows the same anomalies as the hydride. Both α- and β-pinene give the same yield of the same solid chlorhydrate, and thus the hypothesis suggested by Semmler is confirmed.

α-Bromocrotonic Aldehyde.—P. L. Viguier.—Crotonic aldehyde is cooled in a mixture of ice and salt, bromine is added, and the dibromobutyric aldehyde obtained is treated with sodium acetate solution at 150—170°. The product is then distilled in a current of steam. Above 50° bromocrotonic aldehyde passes over, and although the yield is low and the product not very pure this method has the advantage of being very rapid. The bromocrotonic aldehyde thus prepared is the α substance. It condenses with malonic acid to give bromosorbic acid, and with hydrocyanic acid to give bromangelactic acid.

Trinitro-p-anisidine.—Fr. Reverdin.—When benzoyl-*p*-anisidine is nitrated a dinitro derivative of formula—

$$\underset{(1)}{C_6H_2}.\underset{(2)}{OCH_3}.\underset{(3)}{NO_2}.\underset{(4)}{NO_2}.NH.C_7H_5O$$

is obtained. The nitration of this compound gives a derivative which is trinitrated in the nucleus and mononitrated in the benzoyl radical:—

$$\underset{(1)}{C_6H}.\underset{(3)}{OCH_3}.\underset{(8)}{NO_2}.\underset{(6)}{NO_2}.\underset{(4)}{NO_2}.NH.C_7H_4O(NO_2).$$

A crystalline product of formula $C_{14}H_{10}O_8N_4$ is obtained at the same time.

Derivatives of Cholesterine.—L. Tchougaeff and W. Fomin.—Cholesterine is easily transformed into methyl cholesterylxanthogenate, $C_{27}H_{45}—OCS—S.CH_3$. This decomposes at 200° into two isomeric hydrocarbons, which the authors call α- and β-cholesterylenes. Their formula is $C_{27}H_{44}$. They are lævo-rotatory, and possess the normal rotatory dispersion. They decolorise bromine, and fix pure hydrogen in presence of platinum black.

No. 23, June 6, 1910.

Preparation and Properties of β-Dialkyl-α-hydrindones.—A. Haller and Ed. Bauer.—The chlorides of benzyldialkylacetic acids in presence of aluminium chloride condense to form 2.2-dialkyl-1-indanones. The same substances can be prepared more simply from the 1-indanones by treating them with sodamide and alcoholic iodides. However they are formed these dialkylindanones readily regenerate the amide of the benzyldialkylacetic

acid. In order to obtain diethylindanone the authors have prepared the benzyldiethyl and benzylethyl acetophenones, and also the dibenzylethyl acetophenone, which have not been obtained previously.

Oxidising Effects of the Ultra-violet Rays on Gases. Peroxidation of Oxygen Compounds of Nitrogen and Sulphur.—Daniel Berthelot and Henri Gaudechon.—The ultra-violet rays do not make oxygen oxidise free nitrogen; the reaction being strongly endothermic the rays either cannot furnish sufficient energy or energy at the chemical potential necessary for the action to take place. On the other hand, the ultra-violet rays cause the peroxidation of mono- and dioxide of nitrogen; these reactions are almost neutral from a thermic point of view, or else are exothermic. Sulphuric acid is also formed from sulphurous anhydride.

Action of Air on Coal.—P. Mahler.—When coal is subjected to the action of a current of atmospheric air at relatively low temperatures, *i.e.*, below the boiling-point of water, some carbon monoxide is formed, smaller quantities being obtained with damp than with dry coal. Thus carbon monoxide is a normal and not an accidental constituent of the air of coal mines. At higher temperatures some ulmic acid is formed.

Oxidation of Acetylenic γ-Glycols.—Georges Dupont.—When the acetylenic γ-glycols are subjected to oxidation with permanganate, α-acid-alcohols are formed according to the equation—

$$\begin{matrix}R\\R'\end{matrix}>COH-C\equiv C-COH<\begin{matrix}R\\R'\end{matrix}+O_3+H_2O=$$

$$=2\begin{matrix}R\\R'\end{matrix}>COH-CO_2H.$$

Thus the glycol, $\begin{matrix}CH_3\\CH_3\end{matrix}>COH-C\equiv C-COH<\begin{matrix}CH_3\\CH_3\end{matrix}$, gives oxyisobutyric acid. The yields are poor and very variable. If, however, the alcoholic functions are converted into ether oxides or ether salts far more satisfactory results are obtained.

Conversion of Hydroarometic Alcohols into corresponding Phenols.—Léon Brunel.—The hexahydroaromatic alcohols, thymomenthol and carvomenthol, can be made to regenerate the corresponding phenols by oxidation, bromination, and decomposition by heat of the dibrom derivatives. Catalytic dehydrogenation in presence of hot divided copper gives better results. Thus, in the catalytic hydrogenation of phenols containing a branching-chain, like thymol or carvacrol, the chain is unaffected.

MISCELLANEOUS.

Institute of Chemistry.—*Pass List, July Examinations*, 1910.—Fifty-nine candidates presented themselves for the July Examinations of the Institute of Chemistry. Seventeen candidates passed the Intermediate Examination—D. L. Allan, S. W. Bridge, G. M. Carruthers, D. S. Dawson, B.Sc., F. E. Day, B.Sc., G. J. Eastburn, W. J. S. Eastburn, H. D. Elkington, Maud Gazdar, B.Sc., D. Hamilton, G. Hamilton, W. P. Harmsworth, W. Jewell, R. W. Pope, S. P. Schotz, J. Sorley, J. C. White. In the Final Examination, one candidate passed in Mineral Chemistry—C. S. Grace, B.Sc.; one candidate passed in Metallurgical Chemistry—W. A. Riley; ten passed in Organic Chemistry—F. L. Bassett, B.Sc., F. Challenger, B.Sc., F. A. F. Crawford, B.A., E. G. Davis, W. Dickson, J. R. Nicholls, G. C. Petrie, E. F. Pollock, T. Schwarz, T. A. Simmons, B.Sc.; and eight candidates passed in the Chemistry of Food and Drugs, &c.—H. M. Harvey, D. Henville, F. E. Laughton, H. R. Lyell, W. M. Paulley, B.A., P. L. J. Smith, M.A., R. W. Warwick. One candidate passed a Final (A.I.C.) Examination in General Chemistry—J. B. Solomon, A.R.S.M., A.R.C.S.; one candidate passed a Special Examination for the Fellowship—Colin C. Frye; and one Fellow passed in the Chemistry of Food and Drugs, &c.—G. W. Monier-Williams, B.A., Ph.D., F.I.C.

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THE CHEMICAL NEWS.

Vol. CII., No. 2646.

ON SCANDIUM.*

Part II.†

By Sir WILLIAM CROOKES, D.Sc., LL.D., For.Sec.R.S.

Since the publication of the first part of my paper on Scandium (*Phil. Trans.*, A, ccix., 15, March 4, 1908), G. Eberhard, of the Astrophysical Observatory, Potsdam (*Sitzungber. Kgl. Preuss. Akad. Wissensch.*, 1908, xxxviii., 851), reasoning from the fact that the strongest lines of the scandium spectrum are observed in the spectra of stars in diverse stages of development, has come to the conclusion that scandium must be universally distributed on the earth. Investigating the arc spectra of 366 minerals and rocks, he obtained the remarkable result that scandium in small quantities is actually one of the most widely distributed earth elements. He shows that it occurs most frequently in zirconium minerals—in beryls, titanates, columbites, and titanocolumbites of the rare earths—also in micas; and, finally, that specimens of wolframite and tinstone from Saxony and Bohemia contain scandium in sufficient quantity to make its extraction advantageous.

These results of Eberhard were quickly verified by Prof. R. J. Meyer, Berlin University (*Zeit. Anorg. Chem.*, lx., 134, November 17, 1908; and Chemical News, xcix., 85, 97, February, 1909), who, in a preliminary paper, has described experiments on extracting scandia from the Zinnwald wolframite. Prof. Meyer concludes that this wolframite contains from 0·14 to 0·16 per cent of rare earths, and that these rare earths contain 0·30 to 0·33 per cent of scandia. Thus the original wolframite would contain about $0{\cdot}15/100 \times 0{\cdot}315/100 = 0{\cdot}04725/10000$, or about 0·0005 per cent of scandia. Prof. Meyer has worked out two methods of separating scandia from the wolframite rare earths:—(*a*) Precipitation with hydrofluoric acid from an intermediate product in which the scandium has been concentrated by an oxalic acid precipitation, and (*b*) precipitation with hydrofluosilicic acid, or sodium silicofluoride in acid solution. The raw scandia prepared by the above methods still contains small quantities of yttria and ytterbia, particularly if method (*b*) is used. Prof. Meyer says that his scandia, when freed from cerium and yttrium earths, has the atomic weight 45 to 46, and still contains about 1 per cent of thorium. (A mixture of 99·25 parts of scandium with 0·75 part of thorium would have an atomic weight of about 45·5).

On reading Prof. Meyer's paper I examined the felspar and mica which were associated with the parcels of wiikite procured by me from Finland. The felspar contains a small percentage of rare earths, but no trace of scandia could I detect on examining their photographed spectra, the dominant line, wave-length 3613·984, being entirely absent.

The mica was found to contain about 1 per cent of rare earths, and in the photographed spectrum the dominant lines of scandium are plainly visible. From a comparison of the spectra with those taken with the rare earths from wiikite I should estimate the scandia at about half that in the earths of the best black wiikite.

A specimen of wolframite from Zinnwald was found to contain less than 1 per cent of rare earths, and in the photographed spectrum of these earths, the dominant lines of scandium were strong, accompanied by only the faintest trace of yttrium or ytterbium lines.

Through the kindness of a friend, Dr. Wahl, of the Mineralogical Institute, University, Helsingfors, I also obtained the following authentic specimens of minerals from the locality whence my wiikite was mined:—

No. 1. Felspar from the pegmatite vein carrying monazite and the scandium-wiikite. Lokasaari.
No. 2. Monazite from Lokasaari.
No. 3. Black wiikite from Lokasaari, Impilaks.
No. 4. Brown wiikite from Lokasaari.
No. 5. Wiikite from Lokasaari, another specimen.
No. 6. Mica from Hunttila, Impilaks. (Probably from the wiikite quarry).

Of Dr. Wahl's minerals, No. 1, felspar, contained 1·11 per cent of rare earths. On photographing the spectrum only a very faint trace of scandium appeared.

No. 2, monazite, contained 17·15 per cent of rare earths; the photographed spectrum showed no scandium.

No. 3, black wiikite, contained 22·58 per cent of rare earths; the spectrum showed considerable quantities of scandium.

No. 4, brown wiikite, contained 23·77 per cent of rare earths; the spectrograph showed only a small amount of scandium.

No. 5, wiikite, contained 24·85 per cent of rare earths; the photographed spectrum showed considerable quantities of scandium.

No. 6, mica, contained 0·63 per cent of rare earths, which, on spectrographic examination, contained an amount of scandium about equal to that in the rare earths in Nos. 3 and 5.

I have also to thank Dr. A. Hiorth, of Kristiania, for a typical collection of 23 specimens of rare minerals from Norway; the results of examination of most of these specimens have already been given.

The scandia used in the preparation of some of the salts here described was not absolutely pure. Chemically, no other earth could be detected in it, but the spectrograph revealed traces of yttria and ytterbia. These traces could have been removed by one or more operations, but I thought it advisable to leave them in, for the following reasons:—In each operation of purification some loss is unavoidably incurred, and when chemical reactions are insufficient to find the other earths it is not worth diminishing my lessening stock of scandia for the sake of academic purity. The chief reason, however, for leaving these traces in is that they might afford evidence of a difference of behaviour between one earth and another in the presence of some of the acids used. After each quantitative determination the scandia was dissolved in acid and a spectrogram taken to see if yttria or ytterbia were present. The residual earth was then collected from the mother-liquor and a photograph taken of its spectrum. A comparison of the pair of spectra shows at once if any separation has been effected between the earths present. When separation is apparent further experimentation on a larger scale is reserved to a future occasion.

Scandium Iodate,

$$Sc(IO_3)_3 + 18H_2O.$$

Scandium iodate is best prepared by the metathesis of a soluble scandium salt with ammonium iodate. It forms a white crystalline powder almost insoluble in water. After being well washed and dried in the air it contains 18 molecules of water. The water is held loosely; long drying in a desiccator, or exposure to a temperature of 100° and slightly higher, drives some of it off; only by repeated trials with slight alterations of temperature have I obtained certain definite hydrates. There are indications of other hydrates, but I have not attempted to prepare them.

Analysis.

1. 15·483 gr. of 18-hydrate scandium iodate, dried in the air at the temperature of about 15°, were dissolved in hydrochloric acid and heated until chlorine ceased to be evolved. It was then evaporated to

* A Paper read before the Royal Society, January 20 and June 2, 1910.

† The descriptions and analyses of the following salts were communicated to the Royal Society on December 14, 1909, as now printed:—Scandium aurochloride, platinocyanide, iodate, sulphite, malate, malonate, tartrate, racemate, lævotartrate, and mesotartrate.

dryness with excess of acid and dissolved in water. Ammonia in excess was added, and the whole boiled. The precipitated scandia was filtered, washed, and ignited. It weighed 1·229 gr., = 0·7959 gr. of scandium.

2. 17·956 gr. of 18-hydrate were heated carefully until the temperature rose to 250°. At this point the white salt became slightly brown. It weighed 11·265 gr., showing a loss of 6·691 gr. of water.

	Theory.		Experiment.	
			1.	2.
Sc	44·10	4·94	5·14	62·74
$3(IO_3)$ ..	524·76	58·75	94·86	
$18H_2O$ ..	324·29	36·31		37·26
	893·15	100·00	100·00	100·00

Scandium iodate loses three molecules of water when kept for some time in a desiccator, and leaves a hydrate containing 15 molecules of water.

$$Sc(IO_3)_3 + 15H_2O.$$

15·415 gr. of 18-hydrate scandium iodate were dried for some time over sulphuric acid. The 15-hydrate into which it had changed was dissolved in hydrochloric acid and precipitated with ammonia. After ignition the scandia weighed 1·261 gr., = 0·8166 gr. of scandium.

	Theory.		Experiment.
Sc	44·10	5·26	5·30
$3(IO_3)$	524·76	62·54	94·70
$15H_2O$	270·24	32·20	
	839·10	100·00	100·00

When the 18 hydrate scandium iodate is dried for several hours in a vacuum desiccator over sulphuric acid, it loses five molecules of water and leaves a 13-hydrate,

$$Sc(IO_3)_3 + 13H_2O.$$

1. 7·684 gr. of 13-hydrate scandium iodate, prepared as described, were fused with excess of potassium bisulphate; iodine was evolved, and when the whole was in quiet fusion it was allowed to cool. The melt was boiled out with water, an excess of ammonia added, and the resulting scandia separated. It weighed 0·643 gr., = 0·4164 gr. of scandium.
2. 5·537 gr. of 13-hydrate scandium iodate were dissolved in acid, precipitated by ammonia as already described, and the resulting scandia collected. It weighed 0·463 gr., = 0·2998 gr. of scandium.
3. 18·104 gr. of 13-hydrate scandium iodate, dried at 250°, lost 5·205 gr. of water.

	Theory.		Experiment.		
			1.	2.	3.
Sc . ..	44·10	5·49	5·42	5·41	71·25
$3(IO_3)$ ..	524·76	65·35	94·58	94·59	
$13H_2O$.	234·21	29·16			28·75
	803·07	100·00	100·00	100·00	100·00

When the 18-hydrate is heated for some time to 100° it loses eight molecules of water, and leaves a 10-hydrate,—

$$Sc(IO_3)_3 + 10H_2O.$$

20 983 gr. of 10-hydrate scandium iodate, decomposed in the manner already described, yielded 1·907 gr. of scandia, = 1·235 gr. of scandium.

	Theory.		Experiment.
Sc . ..	44·10	5·89	5·88
$3(IO_3)$ ..	524·76	70·06	94·12
$10H_2O$.	180·16	24·05	
	749 02	100·00	100·00

When heated to about 250° scandium iodate loses all its water of crystallisation, and becomes anhydrous,—

$$Sc(IO_3)_3.$$

15·409 gr. of anhydrous scandium iodate were dissolved in acid, precipitated with ammonia, and the scandia collected. It weighed 1·724 gr., = 1·1116 gr. of scandium.

	Theory.		Experiment.
Sc	44·10	7·75	7·24
$3(IO_3)$ . ..	524·76	92·25	92·76
	568·86	100·00	100·00

Scandium Sulphite,

$$Sc_2(SO_3)_3.$$

Scandium sulphite is formed by mixing solutions of scandium chloride and sodium sulphite. It forms a heavy white precipitate, soluble in excess of sodium sulphite when heated, slightly soluble in hot water and insoluble in cold water. The air-dried salt is anhydrous, and has the composition given above.

Analysis.

4·236 gr. of the air-dried salt were dissolved in hydrochloric acid and the solution boiled until sulphurous acid ceased to be driven off. Ammonia in excess was added, and the whole boiled. The scandia was filtered, washed, and ignited. It weighed 1·765 gr. = 1·1430 gr. of scandium.

	Theory.		Experiment.
2Sc..	88·20	26·86	26·98
$3SO_3$	240·21	73·14	73·02
	328·41	100·00	100·00

Scandium Borate,

$$ScBO_3.$$

Scandium hydroxide ground with a solution of boric acid undergoes no apparent change. Slight combination takes place on boiling the mixture, but no definite compound is produced.

Re-crystallised boric acid and scandia were mixed together, the acid being in excess, and the whole heated to bright redness for an hour in a platinum crucible. The mixture fused to a clear liquid, and on cooling the melt was extracted with boiling water, filtered, and washed. The residue on the filter was shaken up with much water, levigated and poured on to a filter, and thus was separated, until only the larger heavy particles were left behind. The scandium borate thus prepared is in the form of a white powder, having the appearance under the microscope of minute transparent spheres. In transmitted polarised light each spherulite shines like a point of light on the dark field when the analyser is crossed, each point alternately disappearing and reappearing as the stage is rotated.

The analysis of the borate at first presented difficulties. It dissolves easily in dilute acids, and on adding ammonia a precipitate, chiefly of scandium hydroxide, is formed, but the hydroxide carries down with it variable quantities of borate. The plan finally adopted was to dissolve the borate in dilute hydrochloric acid and precipitate hot with ammonia. The precipitate was filtered, washed, and dried. The precipitated hydroxide was then ignited in a platinum crucible, hydrofluoric acid was poured on, and it was kept at a gentle heat for some hours. Strong sulphuric acid was added, and the mixture was gradually heated till dry. The residual scandia was then ignited strongly and weighed.

Analysis.

8·037 gr. of scandium borate, treated in the manner described, gave 5·277 gr. of scandia, = 3·4173 gr. of scandium.

	Theory.		Experiment.
Sc	44·1	42·77	42·52
BO_3	59·0	57·23	57·48
	103·1	100·00	100·00

(To be continued).

THE CORRELATION OF ROCK AND RIVER-WATER ANALYSES.

By H. S. SHELTON.

The analysis of rocks, and of the substances dissolved in river-waters, tends to become a mechanical process, and to be undertaken for diverse and special purposes, without due regard to the broader scientific aspects. One point in particular has not received the requisite attention. It is not sufficiently recognised among analysts that, between the analyses of rocks and of the dissolved matter in river-waters there must be an intimate correlation. The solid matter in solution is, in the main, obviously derived from the erosion of the rocks. If therefore any soluble substance widely distributed in rocks fails to show a due equivalent in river-water analyses, the matter calls for investigation. If, on the other hand, any widespread constituent of river-water, not to be accounted for in other ways, is found only in minute proportion in the rocks, there must be serious errors either in rock analyses, or in water analyses, or in both. Although some attempts have been made to correlate river-water analyses with the geologic formation of the districts in which the analyses have been taken, there appears, as yet, to have been no serious effort to follow the dissolved constituents of river-waters to their origin in the rocks (see Hanaman, "Analysis of Bohemian Waters," quoted by Clarke; "Data of Geochemistry," p. 79).

The present paper is not concerned with the correlation of particular formations with particular rivers, but with the broad average analyses of river-waters. It is a preliminary survey of the ground, in order to see whether every substance which appears in sensible proportion in water analyses can be identified with a corresponding widespread constituent in the rocks. A good statistical average, which will serve the purposes of this paper, has been compiled by Sir John Murray. His average of the substances in solution in the great rivers of the world, though it was made more than twenty years ago, and is open to criticism in detail, is the best extant, and any errors it may contain are probably confined to minor details and proportions (*Scottish Geogr. Mag.*, 1887, "Data of Geochemistry," p. 88). This estimate, reduced to ionic form by Prof. Clarke, is quoted below.

	Per cent of inorganic solid.
CO_3	41·33
SO_4	8·22
Cl	1·85
NO_3	2·82
Ca	20·46
Mg	4·65
Na	3·47
K	1·33
SiO_2	10·75
Al_2O_3, Fe_2O_3	4·76
Minor constituents	0·36
	100·00

Organic matter 10·37 per cent of total solid.

To show the general correlation between these constituents of river-waters and the composition of the rocks, it will be convenient to quote the result of the most recent and the most thorough series of rock analyses that has ever been undertaken. This table of Prof. Clarke contains not only an account of the analyses undertaken, but a weighed statistical average, making due allowance for the abundance or rarity of the various types of rocks included in the average ("Data of Geochemistry," p. 31).

	Igneous rock.	Shale.	Sedimentary rock (sandstone).	Limestone.
SiO_2	59·87	58·1	78·33	5·19
Al_2O	15	15·4	4·77	0·81
Fe_2O_3, FeO ..	5·98	6·47	1·37	—
MgO	4·06	2·44	1·16	7·89
CaO	4·79	3·11	5·55	42·57
Na_2O	3·39	1·31	0·45	0·05
K_2O	2·93	3·24	1·31	0·33
Water	1·86	5	1·63	0·77
CO_2	0·52	2·63	5·03	41·54
S	0·11	0·26 (*a*)	0·07	0·11
Combined oxygen	—	0·38	—	—
Other minor constituents (*b*) ..	1·47	1·66	0·33	0·74
Total ..	100·00	100·00	100·00	100·00

(*a*) Expressed as 0·64 SO_3.
(*b*) Containing a large proportion of titanium.

To show the relation of these tables to the problems of erosion and of rock solution, it is necessary to state that sandstone, shale, and limestone are estimated to occur, in the area subject to erosion, in the relative proportions of 80, 15, and 5. The proportion of igneous rock in the part of the earth's crust subject to erosion is somewhat more uncertain, but it is usually estimated as about one-quarter of the sedimentary. The presence of metamorphic formations, which may arise both from igneous and from sedimentary rocks, makes exact calculation impossible. For the same reason, a general average of all rocks subject to erosion cannot readily be made; but a study of the tables will show that, within the limits of statistical error, this differs only from the composition of igneous rock in a deficiency of sodium and an excess of carbon, both of which differences are readily explained.

In a preliminary rough survey, which is all that is possible in the present paper, we must first of all note the constituents of river-waters which can have any origin other than that of solution of the rocks. The proportion of carbonate is undoubtedly largely due to atmospheric carbon-dioxide, which is continually renewed volcanically, and to the special solubility of calcium carbonate in carbon-dioxide solution. The latter remark also applies to the remarkable percentage of calcium. The nitrate is probably over-estimated; but what proportion exists we can refer to decaying organic matter. The chlorine, a portion of the sodium, and a minute proportion of magnesium and of other salts, is due to the precipitation of sea-salt in the rain.

Making these necessary allowances, a rough comparison of the two tables will show that nearly all the constituents found in sensible proportion in river-water—calcium and magnesium carbonates, iron and alumina, sodium potassium, and silica are found in large proportion in the igneous and sedimentary rocks. Moreover, no considerable constituent of the rocks is missing from the river-water table.

One substance found in river-water analyses I have already discussed at some length in a previous paper (Chemical News, 1909, xcix., 253). To those remarks, and to the suggestions contained therein, I will merely add the expression of opinion that, in the ordinary water analysis the sodium is over-estimated. Theoretical reasons for that opinion are confirmed by the fact that the statistical abstracts which record only the work of well-known and careful analysts (*cf.* Dubois, *Proc. Amsterdam Acad.*, 1904)

show a smaller percentage of sodium than those which include indiscriminately all published results.

To the law of correlation laid down in the preceding paragraphs there is one, and only one, outstanding exception. The proportion of sulphate, which is exceeded in river-water analyses by calcium carbonate and silica only, is not contained in the rocks in any sensible proportion. In view of the startling nature of the discrepancy, it will be convenient to investigate it in some detail, and to inquire what sources are possible for the enormous proportion of sulphate stated by analysts to be present in river-waters. So large is the proportion that we can show the need of correlation by assuming that all the sulphides in the rocks are oxidised and carried to the sea as sulphates. Making this outside assumption, we are still unable to account for the sulphate, as can be shown by the following line of reasoning:—The ratio between the solids carried to the sea in suspension and that carried in solution is uncertain; but it is almost certainly not greater than 4 to 1 (see Appendix). Accepting this estimate, it follows that any constituent which cannot be otherwise accounted for must be present in the rocks in at least one-fifth the proportion of total solid that is shown in river-water analyses. This is a minimum which would never be actually reached, because, in reality, every element is included, more or less, in the solid carried to the sea in suspension. Our 8·22 per cent of sulphate, or 2·74 per cent of sulphur, thus implies that more than 0·5 per cent of the earth's crust subject to erosion, or its equivalent in some other form, must be the element sulphur. As the actual proportion of sulphur is said to be little more than 0·1 per cent, and, even in the shales where it is highest, is less than 0·3 per cent, we can show the discrepancy in a most glaring form.

I have not thought it necessary to make new tables, because the examination of water analysis tables invariably shows that there is no considerable error in Sir John Murray's statistics. On the other hand, the examination of the analyses on which Prof. Clarke's weighed estimates are made (see *Bull.* Nos. 148, 168, 228, 330, U.S. Geol. Survey) only indicates the difficulty of discovering from what sources even his small proportion of sulphur has been obtained. In the igneous and metamorphic rocks it is found only combined with iron, and, in the sedimentaries, apart from deposits of gypsum, usually associated with salt-beds, its occurrence appears to be confined to a few bituminous shales. The examination of these analyses makes it probable that non-magnetic substances are included in the estimate; but in order to deal with the subject exhaustively we will note these and other possible subsidiary sources.

The beds of gypsum and localised deposits of pyrites and other minerals can be briefly disposed of. Gypsum is usually found associated with salt, and cannot be much more widespread. On this point the chlorine researches of Jackson will throw some light. He has shown that, even in New York State, noted for brine springs, the effect on the chlorine content of river-waters is infinitesimal (see "Normal Distribution of Chlorine," p. 10). In view of the larger proportion of sulphate, and the smaller solubility of gypsum, we are safe in ignoring the latter substance.

The oxidisation of local deposits of sulphides can similarly be ignored. At first sight the imposing list of ores containing sulphur is liable to blind chemists to the fact that the sum total of the extravasated and non-magnetic substances is infinitesimal compared with the igneous and sedimentary rocks. Of the minerals, the sulphides are not the most widespread. All, indeed, are rare, with the exception of pyrite and pyrhotite, which are mainly local segregations in igneous rock, and, as such, already accounted for. They are, moreover, rare compared with other iron minerals.

The only other possible source is rain-water. Analysis always shows a minute proportion of sulphate, but the balance of evidence tends to show that this proportion, except in the immediate neighbourhood of a large town, is very much smaller than the chloride, and is not much greater than that which can be accounted for cyclically by deposition of sea-salt (see Appendix).

All these infinitesimals add up to but a minute amount. It is doubtful whether their total will account for one-tenth of the sulphate stated by analysts to be carried by the rivers to the sea. Our investigation therefore shows clearly that the discrepancy is great and glaring, and cannot be accounted for by statistical error. Estimating all possible sources at their highest, more than half of the river-water sulphate is unaccounted for. We can therefore certainly infer that there is either a considerable error in sulphur determinations of rock analyses, or in the sulphate determinations of river-water analyses, or in both.

This conclusion is all I venture to put forward with certainty. I propose, however, to put forward my own theory of the cause of the discrepancy, without claiming for my explanation the same high degree of probability that I attribute to the previous statement. It is a hypothesis that must be confirmed or rejected by subsequent careful experimental work. Nevertheless, I consider the theory well worth the serious attention of analysts.

There are good reasons for thinking that the error lies, not with the sulphur determinations of the rocks, but with the sulphate analyses of the river. Of these I will give only one. The sulphate in the sea would be accumulated in a comparatively short time compared with that of other oceanic salts, and, contrary to a widespread impression, there is no evidence that any appreciable proportion is deposited on the ocean floor (see Appendix). I therefore suggest that a considerable proportion of so-called sulphate in river-waters is not sulphate at all.

It seems to me most probable that analysts, following the methods recommended in all the best text-books (see Wanklyn, "Water Analysis," eleventh edition, p. 123; Thresh, pp. 249 *et seq.*) found a soluble substance giving a barium salt insoluble in hydrochloric acid, and immediately concluded that the precipitate was sulphate of barium. It seems to me probable that, while there will probably, in most waters, be sufficient sulphate to show a qualitative test, a considerable proportion of the so-called barium sulphate is, in reality, a substance found more commonly in the earth's crust. We know, for example, that fluosilicic acid has an insoluble barium salt. This may possibly be present to a minute extent, but it is well worth investigation whether other complex silicates, and particularly the compounds of silica with the humus acids of the soil, may not possess the same property.

One further reason for thinking the presence of organic silicates a probable solution is that, as stated in the usual analyses, both silica and sulphate are more variable than other constituents. In a previous paper (CHEMICAL NEWS, 1909, xcix., 253), when discussing the subject of sodium analyses, I stumbled across an instance, in two otherwise fairly consistent analyses of the same river at the same place, where the sulphate in the one was stated as five times as great as in the other. The silica is also irregular. Though usually occurring in small proportion, it sometimes—even in the work of the most accurate manipulators—is found to be the largest soluble constituent. Thus, Deville on one occasion found more than 20 per cent in the Rhine, instead of the usual 2 per cent. The reason for variation in the proportion of silica is obvious, in that it depends on the humus acids of the soil, and would therefore be seasonal. On the other hand, there is no reason why true sulphate should be more variable than any other soluble constituent. It therefore seems not improbable that the two commonly occurring irregularities may be due to the same cause, and that, according to methods of analysis or variation in the actual compound present, silica may show itself in analyses either as silica or as pseudo-sulphate.

Not being myself engaged in analytical investigation, I desire to call the attention of analysts in all parts of the world to the portion of soluble matter commonly called sulphate, and I suggest that large quantities of this residue should be obtained and subjected to thorough analytical investigation.

Appendix (Numerical Data).

A. *Rate of Erosion.*

1. *By Sediment.*—Ganges Basin, 1/823 foot per year. Mississippi Basin, 1/6000 foot per year (Geikie, *Geology*, i., 589). Average, 1/2400 foot per year (Sollas). This is probably an overestimate.

2. *By Solution.* England and Wales, 1/13000 foot per year (Mellard Reade, "Chemical Denudation," preliminary table).

The rate of solvent denudation is variable, and is to some extent dependent upon sedimentary denudation, but the proportionate variation is not so large.

B. *Calcium Sulphate on Ocean Floor.*

It has been stated by Prof. J. Joly that large quantities of calcium sulphate are deposited on the ocean floor (*Trans. Roy. Soc. Dublin*, 1899, p. 37). There are good reasons for doubting this statement. An examination of the analyses of the *Challenger* muds gives the following interesting result. Omitting phillipsite, manganese nodules, phosphatic concretions, sharks teeth, and whales' ear-bones, there are 83 analyses. The proportion of calcium sulphate is shown in the following table:—

Total analyses	83
$CaSO_4$, nil	24
Trace	2
Less than 0·5 per cent	22
Less than 1 per cent..	26
Less than 2 per cent..	9
Over 2 per cent	2

The 11 analyses showing a proportion greater than 1 per cent comprise 3 red clays, 5 globerigina ooze, 1 greensand, and 2 volanic mud. These, it will be noted, are porous materials. The wide presence and consistently minute quantity is suspicious. The most probable explanation is that, after washing the specimen with water, the chlorides and soluble salts contained in the sea-water would be removed. On the other hand, a variable quantity of the more insoluble calcium sulphate, which, on the drying of the specimen, would adhere to the mud, probably survived the process of washing. It will also be noted that nearly all the analyses showing calcium sulphate were carried out by one analyst.

C. *Sulphates in Rain-water.*

If all the sulphate in rain-water were cyclic, the amount would then be one-seventh of the chlorine (Clarke, "Data," p. 95). The actual amount is usually greater. This result is to be expected theoretically, because of the decay of vegetable matter, the burning of coal in large towns, and for some other reasons. Analyses of rain-waters varies greatly. Angus Smith ("Air and Rain," p. 266) gives the sulphate 0·1134 of the chloride. Warington (*Journ. Chem. Soc.*, 1887) finds the sulphate slightly greater than the chlorine. The same author warns analysts that gas-fumes are a very probable source of sulphuric acid, a remark that may be commended to analysts finding more than an infinitesimal proportion of sulphates (*Journ. Chem. Soc.*, 1889, p. 545). The evidence is doubtful and conflicting, but there is no reason to assume that rain-water supplies more than a small proportion of river-water sulphate.

Other Analyses.

1. Lincoln, New Zealand. Cl, 7·74 per million; SO, 2·01 per million (Clarke's "Data," p. 47).

2. St. Pierre, Normandy. Sulphate less than half chloride (*Ibid.*, p. 48).

3. Garforth, Yorks. The sulphate was found to be as high as 11 parts per million, three times the amount of the chloride. If this is not an error, due to gas flames and other causes, it is probably to be explained by the number of manufacturing towns in the neighbourhood (*Chemical Society Abstract*, 1909, p. 340).

D. *Instances of Abnormal Proportions of Silica in River-waters.*

	Analyst and reference (Clarke's "Data").	Date.	River.	Per cent silica.
1.	F. C. Robinson (p. 62) ..	1905	Androscoggin	23·5
2.	Dole and Roberts (p. 63).	1907	James	26·32
3.	E. E. Slosson (p. 67) ..	1895	Laramie	31·73
4.	Kyle (p. 74)	1878	Uruguay	46·22
5.	Deville (p. 76)..	1848	Rhone	31·59

In all these cases the total salinity is normal.

DISCUSSION OF AN ARTICLE BY Mr. A. H. PATTERSON ON "THE PROBABLE ELECTRICAL NATURE OF CHEMICAL ENERGY."

By J. E. MILLS.

Recently there appeared in the Chemical News (1910, ci., 115) a paper under the above title containing some comment upon, and criticism of, an article on "Chemical Energy" by the writer (*Trans. Am. Electrochem. Soc.*, 1908, xiv., 35). I duly published a reply (*Ibid.*, 1909, xv., 586) to Mr. Patterson's comments, and the article below is largely taken from that discussion.

The calculation by Mr. Patterson of the "potential energy of charge" on 16 grms. of oxygen and 2·016 grms. of hydrogen from the view-point of the electron theory is very interesting. Overlooked both by Mr. Patterson and myself a similar calculation had previously been published by Svante Arrhenius ("Theories of Chemistry," 1907, p. 63). While the energy charge so calculated can only be regarded as an estimate, yet it is extremely interesting to note that this estimate amounts to 640,000 calories (Arrhenius obtains 636,120 calories), and that only 67,300 calories are given out by the three reactions:—

$$H_2 = H + H$$
$$\tfrac{1}{2}O_2 = \tfrac{1}{2}(O + O)$$
$$H + H + O = H_2O.$$

This seems to indicate a condition of affairs exactly in accord with the idea that I had already expressed, namely, that the atoms HOH while in the form of water (ice) yet possess a vast amount of energy. I am not in the least surprised that the amount retained should be ten times the amount liberated.

As regards the "residual attraction," I believe that the molecular attraction is probably the residual chemical attraction, being caused by stray lines of force, and while I agree in the main with Mr. Patterson's observations upon the residual attraction, I do not believe that the "electron" theory aids in understanding its mechanism. The number and intensity of these stray lines of molecular force will always be dependent *mutually* upon the atoms which make up the molecule, and no one sided argument, such as the one quoted from Prof. Thomson, as indicating that the residual attraction of carbon is greater when it is positively than when it is negatively electrified, has much weight. Not only because it is one-sided, failing to consider the action as mutual, but because "a" is no measure of the molecular attraction in the sense used.

As regards "electrical conduction," the electron theory considers that electricity is conveyed:—

1. In a solution by *ions* moving in *both* directions.
2. In a metallic conductor by *electrons* moving in *one* direction.
3. In a molten salt by *ions* moving in *both* directions.
4. In a gas under ordinary pressure by *ions* moving in *both* directions.
5. In a gas under greatly reduced pressure (vacuum-tube discharge) by *electrons* moving in *one* direction, and *positively charged atoms* moving in the *other* direction.

I, for one, will confess frankly that I am not satisfied with a theory of electrical conduction that jumps about at will from electrons to ions, if the usual meaning be attached to those terms. I believe that electricity will be conducted in a gas, in a metal, in a molten salt, and in a solution, in a precisely similar manner so far as the inner mechanism of that conduction is concerned. I attempted in my former paper to state only one of the conditions upon which this conduction depended. I stated :—"The essential requisite appears to me to be a free, that is, an unabsorbed attraction." I had no idea of leaving the impression that the conductivity depended only upon this condition. I regarded this condition merely as *one essential factor*, and I discussed this factor alone, because it was this special feature of electrical conductivity that touched the subject I was discussing (chemical energy). I do not pretend to know all of the factors upon which electrical conductivity depends. But, to clear up any ambiguity, I would state what I consider to be one other factor; in conductlng electricity the *atoms must move*. That is, not only must they have a free, that is, an unabsorbed or indefinitely absorbed, attraction (an attraction which does not bind them definitely to other particular individual atoms), but they must move while they conduct the current.

The electron theory admits the movement of the ions as a necessary part of the conduction in a solution, in a molten salt, and in a gas under ordinary pressure. In a gas under reduced pressure it does not wholly deny the movement. But to explain metallic conduction and the vacuum-tube discharge, the idea of electrons is introduced. As regards metallic conduction, I would point out that liquid mercury is a metal and conducts as a metal. Now, if a very large current be passed through the mercury, the motion of the mercury becomes visible and the mercury heaps itself around the electrodes, and finally the "pinch" phenomenon is observed. This phenomenon is similarly observed with other metals. The explanation which has been suggested of this pinch phenomenon as induced by a stress in the ether should not be allowed to conceal the fact that we have here very clear evidence that the atoms of mercury are in motion towards the electrodes. Moreover, we have evidence in every case of metallic conduction that the conduction is accompanied by increased atomic motion, *for the metal becomes heated*. Mr. Patterson says :—"The kinetic energy of these moving electrons smashing, as it were, into the atoms, causes increased atomic motion, and the wire becomes heated." Why not drop out the electron clause and confine our attention to the fact that *always*, be it solution, metal, salt, or gas, when a current passes, the atomic motion is disturbed?

My belief that in all electrical conduction the atoms move is founded not only upon the fact as an independent observation, but is likewise a direct deduction from my statement that an essential requisite of electrical conduction is a free attraction. I think this "free" attraction is an essential requisite, probably *because the atoms must move with reference to each other in order to conduct*. So long as the atoms are bound hard and fast to one another and we have no "free" attraction, they cannot move with the freedom necessary to conduct the current, and the body is a non-conductor. And I would again point out what I said before, that the metals are the best conductors *because* they are *mon*atomic, the atomic attraction being free or unneutralised; that bismuth, carbon, sulphur, &c., are poorer conductors because their molecules are complex and the atoms are more or less bound to one another; that an oxide, or salt, or gas, is a non-conductor just so long as it remains a perfectly definite chemical compound.

Mr. Patterson says :—"It is difficult on this (my) hypothesis to see why mercury, for example, should not be a better conductor than silver, as its atoms seem to be less firmly bound together; nor why the resistance of selenium should change so marvellously with the degree of illumination to which it is subjected; nor why increase of temperature, which drives atoms further apart, should not always increase conductivity, nor how the vacuum-tube discharges and the action of electric values may be explained; nor how the change of resistance of bismuth in a magnetic field may be accounted for." I would invite Mr. Patterson to give a soul-satisfying explanation of these phenomena in terms of the electron theory.

From my point of view I can calculate the attraction of the atoms of mercury for each other, but the data is lacking for silver, and I cannot therefore compare the molecular attraction of the two metals. But the motion of the atoms, as well as the attraction which also varies with the distance apart of the atoms, are factors to be considered, and I could not, were the attraction known, predict the conductivity.

The change of the resistance of selenium upon exposure to the light, and of bismuth in the magnetic field, are understood by nobody on earth so far as I know. But these changes certainly do indicate a remarkable change in the "phase" of the selenium and bismuth, and it is a well known and legitimate inference that a variation in nearly all the properties of both selenium and bismuth must take place at the same time.

My point of view does not necessitate the conclusion that driving atoms further apart always increases the conductivity. Even if I were to grant that the amount of "free" attraction was thereby increased, it must also be remembered that the atoms *must move and move further* as they conduct. Moreover, driving atoms further apart should be carefully distinguished from driving molecules further apart.

As regards the vacuum-tube discharge, I had no intention when my paper on chemical energy was written of discussing that phenomenon at all. But I feel now that it is necessary for me to make my position clear. I am a hearty believer in the probable identity of electrical and chemical forces. Or, more clearly expressed, I believe that both electrical and chemical phenomena are caused by a *definite amount of potential energy belonging to an atom*. The part of the electron theory in which I do not at present believe is that this definite amount of potential energy can exist *independently of the atom*. That is to say, I do not believe that the attractive force (electrical or chemical, as you prefer), or the potential energy of which it is a manifestation, which I conceive of as proceeding from an atom in all directions, can be rolled into a ball and detached from the atom and exist independently as a corpuscle or electron.

The actual nature of chemical (electrical) energy is a very fundamental question. The nature of mass, of matter, of energy, and of their relations, must all be considered at the same time. Now, in my paper on chemical energy, after tabulating the main characteristics of the various attractive forces, I expressed the view that any attractive force (f) could be measured by :—

$$1.\quad f = K\frac{\text{Amount of attraction absorbed at unit distance} \times \text{Amount of attraction absorbed at unit distance}}{d^2}$$

d being the distance apart of the attracting particles.

Now, the gravitational force (f') in ordinary terminology* is measured by :—

$$2.\quad f' = K'\frac{\text{Mass} \times \text{mass}}{d^2} = K'\frac{m\,m'}{d^2}$$

and the electrical attractive force (f'') of two electrically charged masses by—

$$3.\quad f'' \quad K''\frac{\text{Charge} \times \text{charge}}{d^2} = K''\frac{e\,e'}{d^2}.$$

Now, suppose the gravitational force and the electrical force to be *really identical*. That is, suppose the so-called gravitational, chemical, molecular, electrical, and magnetic

* I think the gravitational energy of a molecule should be regarded as definite in amount and as belonging to the molecule. The law of gravitation from this point of view is best expressed by, force $= Km/d^2$. Similarly for the other forces. I cannot discuss this question here, and therefore use the ordinary terminology.

forces are really only manifestations of one and the same fundamental attraction. Then we have—

$$4.\quad f' = f'' = K'\frac{m\,m'}{d^2} = K''\frac{e\,e'}{d^2} \text{ and } \frac{e\,e'}{m\,m'} = \text{constant.}$$

a condition which is satisfied if—

$$5.\quad \frac{e}{m} = \text{constant} \quad \text{and} \quad \frac{e'}{m'} = \text{constant.}$$

Thus, from my point of view, I am led to a fundamental discovery of the modern electrical theory, that the ratio of a charge on a body to its mass is a constant. But the interpretation which I must give to this fact is entirely different from the interpretation usually given, for my method of derivation leads me to conclude that the mass of a body varies with the amount of the attraction absorbed at unit distance, and that both mass and charge are relative and not absolute properties. Therefore I do not have to conclude that an electron is a small particle always with a mass about one-thousandth that of a hydrogen atom. I am rather inclined to believe that the hydrogen atom, or any other atom, may itself act as and become an electron.

There are at present, even in my own mind, a good many question marks surrounding the above conclusion, and I do not wish to mislead any one. I am at present engaged in revising the papers upon molecular attraction and attractive forces which have led to this belief, and a complete statement of the reasons for my views will be given in that revised paper.

To a further statement by Mr. Patterson* I would only say that I have never denied the possible existence of electrons. In common with nearly all chemists, influenced largely by the relations shown in the Periodic Table, I have always supposed that the atoms are complex. There may be removable parts, and electrons may be a suitable name for one of these parts. I only stated, slightly changing the order of the words:—"The part of the electron theory in which I do not at present believe is that the *definite amount of potential energy belonging to an atom* can exist independently of the atom as an electron." I have nowhere in this or any other paper admitted an inability to explain the meaning of the term "unabsorbed attraction," or thought that the existence of electrons would seriously interfere with my views on electrical conduction which caused this discussion. The closing words of my paper on chemical energy state my meaning and position clearly:—"Atoms whose lines of force radiate out indiscriminately to other atoms are good conductors. Atoms whose lines of attractive force extend to certain other definite atoms, the attraction of each being mutually saturated thereby, are very poor conductors."

Camden, South Carolina, U.S.A.,
July 2, 1910.

Oxidation of Aluminium Amalgam.—P. Roger-Jourdain.—The oxidation of aluminium amalgam yields alumina which contains chemically combined oxygen and carbon dioxide, the gases not being simply occluded as the author thought previously. Probably a mixture of aluminium, carbonate, and peroxide is formed. The action takes place only in moist air. The alumina dissolves in acids with effervescence, the carbon dioxide is evolved, but all the oxygen goes to form hydrogen peroxide, which can be directly determined with permanganate.—*Comptes Rendus*, cl., No. 24.

* "I hardly think it necessary to answer Dr. Mills, as my paper is as clear as I can make it in so brief a space. Dr. Mills refuses to admit the existence of electrons independent of atoms, which is, I consider, a demonstrated fact. He further uses as the basis for his whole argument the conception of an 'unabsorbed attraction,' and I cannot grasp this conception in a definite way. He admits that he cannot at present give it a definite meaning, and also admits that if electrons are proved to exist as separate entities outside of atoms, his theory is practically shattered. That is the crux of the situation as between his theory and the electron theory."—*Trans. Am Electrochem. Soc.*, 1909, xv., 591.

THE FRIEDEL AND CRAFTS REACTION WITH CHLORIDES OF UNSATURATED ACIDS.*

By E. P. KOHLER, G. L. HERITAGE, and M. C. BURNLEY.

(Concluded from p. 66).

Experiments with Phenyldibrompropionyl Chloride.

Preparation of the Chloride.—We found the method of preparation used by Collet—addition of bromine to cinnamyl chloride—unsatisfactory, because it is extremely difficult to get a product free from unsatured chloride in this manner. We therefore added bromine to cinnamic acid in the usual way, suspended the dibromide in phosphorus oxychloride, and gradually added a slight excess of phosphorus pentachloride. The resulting chloride could not be distilled without decomposition, but the chlorides of phosphorus were easily removed by heating to 150—160° under diminished pressure. The colourless solid obtained in this way can be purified by crystallisation from dry carbon bisulphide and ligroin, but we found that in our experiments, the crude and pure preparations gave the same results.

Action of Aluminium Chloride.—Our preliminary experiments showed that reactions with phenyldibrompropionyl chloride are accompanied by liberation of bromine. We therefore studied the behaviour of this substance in the presence of aluminium chloride alone. For this purpose one molecule of aluminium chloride was gradually added to a solution of the acid in carbon bisulphide that was cooled in a freezing mixture. A slow but steady evolution of gas commenced almost immediately, and the colour of the solution soon showed the presence of free bromine. The evolution of gas continued for about twenty-four hours, during which the temperature was allowed to rise very gradually to 15°. Repeated analyses of the gas showed that at all stages of the reaction it consisted of hydrobromic acid mixed with a little hydrochloric acid.

The product of the reaction was poured into iced acid, separated, washed, and dried, in the usual way. The ethereal solution was then distilled from a water-bath, first under ordinary pressure, and finally under 12 mm. The distillate contained, besides carbon bisulphide and ether, a small quantity of phenylacetylene—identified by its copper derivative—and a somewhat larger quantity of bromstyrene recognised by its odour and boiling-point. The yellow residue was digested with cold ether. This left a considerable quantity of a sparingly soluble acid, which was purified by re-crystallisation from boiling acetone, and thus obtained in long colourless needles melting at 255°.

Analysis.

I. 0·1799 grm. substance gave 0·3134 grm. CO_2 and 0·0481 grm. H_2O.

II. 0·1471 grm. substance gave 0·2564 grm. CO_2 and 0·0376 grm. H_2O.

	Calculated for $C_9H_7O_2Br$.	Found. I.	Found. II.
C	47·57	7·51	47·53
H	3·08	2·97	2·84

The sodium salt of the acid was readily oxidised with aqueous permanganate, and gave a new acid which melted at 251°, and was identified as *p*-brombenzoic acid by comparison with a specimen on hand. The unsaturated acid was therefore *p*-bromcinnamic acid, previously made by Gabriel, who gives the melting-point 253°.

The filtrates from the *p*-bromcinnamic acid on dilution with ligroin deposited a mixture of acids that was finally separated into cinnamic acid about 20 per cent, α-bromcinnamic acid about 50 per cent, and a small quantity of a new acid that separated from benzene in stout prisms that melted at 172°.

* From the *American Chemical Journal*, xliv., No. 1.

Analysis.

I. 0·1733 grm. substance gave 0·2552 grm. CO_2 and 0·0422 grm. H_2O.

II. 0·1423 grm. substance gave 0·2127 grm. CO_2 and 0·0327 grm. H_2O.

	Calculated for $C_9H_8O_2ClBr$.	Found. I.	Found. II.
C	40·98	40·22	40·75
H	3·03	2·70	2·54

The acid has the composition and chemical properties of an α-brom-ββ-phenylchlorpropionic acid; it gives benzoic acid on oxidation with potassium permanganate, α-bromcinnamic acid and potassium chloride when boiled in alcoholic solution with potassium acetate, and α-brom-,β-phenyllactic acid when digested with hot water. The acid is different, however, from the known substance of this composition and structure; it melted 10° lower, and a mixture of the two began to melt 20° to 25° below the lower melting component. The ether-ligroin from which all acids had been removed by extraction with sodium carbonate left after evaporation a small quantity of non-acid substances that were not identified.

These results show that aluminium chloride removes both hydrobromic acid and bromine from phenyldibrompriopionyl chloride, and that action takes place slowly even at the temperature of a freezing mixture. The effect must be due to the phenyl group in the β-position, because dibrompropionyl chloride forms a double compound with aluminium chloride which is perfectly stable at the ordinary temperature.

Phenyldibrompropionyl Chloride and Benzene.—After trying various methods of procedure, we adopted the following:—Sixty grms. of ground aluminium chloride were added to a solution 121 grms. of the acid chloride and 50 grms. of benzene in 250 cc. of carbon bisulphide. The mixture was kept at −20° for twenty-four hours, and then poured into iced hydrochloric acid. The carbon bisulphide layer on evaporation deposited a solid that was purified by re-crystallisation from absolute alcohol. It gave 63 grms. of a substance that separated in very pale yellow needles melting at 89—90°. This is evidently the product that had previously been obtained from the same reaction by Collet. Our analysis shows, however, that it is not phenyldibrompropiophenone:—

0·1879 grm. substance gave 0·4295 grm. CO_2 and 0·0646 grm. H_2O.

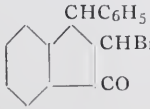
	Calculated for $C_{15}H_{11}OBr$.	Found.
C	62·71	62·33
H	3·83	3·76

The molecular weight was determined in boiling acetone (K = 1710).

Solvent. Grms	Substance. Grms.	Elevation of boiling-point.	Molecular weight.
42·53	0·6274	0·089	285
42·53	1·1752	0·153	285
42·53	1·4925	0·202	262
Calculated for $C_{15}H_{11}OBr$			287

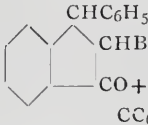
The substance slowly reduced a solution of potassium permanganate in boiling acetone. The sole organic oxidation product was *o*-benzoylbenzoic acid, which was identified by an analysis, by the melting-points of the hydrous and anhydrous acids (90° and 120°), and by the melting-point of the oxime, 162°.

These results prove that the substance is an indene derivative, the oxidation taking place in accordance with the equation:—

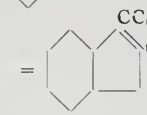


$+ 4O = C_6H_5COC_6H_4CO_2H + HBr + CO_2.$

2-Brom-3-keto-1-phenyl-2.3-dihydrindene reacts readily with organic and inorganic bases, and also with potassium acetate, but it is difficult to isolate pure substances from the products. The substance is most easily identified by means of the semi-carbazone obtained by adding an aqueous solution of semi-carbazide hydrochloride and potassium acetate to an alcoholic solution of the ketone:—



$+ NH_2CONHNH_2.HCl + 2CH_3CO_2K =$



$+ KCl + KBr + 2CH_3CO_2H$

Analysis.

0·1378 grm. substance gave 0·3675 grm. CO_2 and 0·0645 grm. H_2O.

	Calculated for $C_{16}H_{13}ON_3$.	Found.
C	73·0	72·77
H	4·9	5·20

The unsaturated semi carbazone separates in minute yellow needles which, after re-crystallisation from alcohol and acetone, melt with decomposition at 212°. The same substance is formed when the yellow oil, obtained by boiling the halogen compound with alcoholic potassium hydroxide, is treated with semi-carbazide.

Phenyldibrompropionyl Chloride and Brombenzene.—The reaction takes place much more slowly than the corresponding reaction with benzene, and consequently leads to the formation of a larger quantity of acid by-products due to the interaction of the acid chloride and aluminium chloride. These acid products were removed by extraction with sodium carbonate. The extracted solution, on dilution with ligroin, deposited a solid which, after repeated crystallisation from chloroform and absolute alcohol, melted at 143—144°. The substance crystallises in colourless needles, sparingly soluble in ether and alcohol, readily in acetone.

Analysis.

0·1518 grm. substance gave 0·2762 grm. CO_2 and 0·0358 grm. H_2O.

	Calculated for $C_{15}H_{10}OBr_2$.	Found.
C	49·18	49·55
H	2·70	2·66

The bromine compound reduces potassium permanganate dissolved in acetone—slowly at the ordinary temperature, rapidly near the boiling-point of acetone. The sole organic oxidation product is *p*-brom-*o*-benzoylbenzoic acid. This was purified by crystallisation from methyl alcohol. It separated in large flat needles or plates melting at 174°.

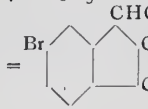
Analysis.

0·1540 grm. substance gave 0·3109 grm. CO_2 and 0·0436 grm. H_2O.

	Calculated for $C_{11}H_9O_3Br$.	Found.
C	55·08	55·06
H	2·96	3·14

These results prove that the principal product of the reaction between phenyldibrompropionyl chloride and brombenzene is 2.6-dibrom-3-keto-1-phenyl-2.3-dihydroindene, an indene derivative with bromine in each nucleus:—

$C_6H_5CHBrCHBrCOCl + BrC_6H_5 =$



$+ HCl + HBr.$

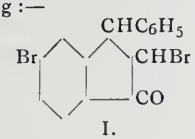
The filtrates from this compound contained another solid product that was isolated with difficulty, but finally obtained in large colourless prisms melting at 86°. This substance was readily soluble in acetone and ether, moderately in alcohol.

Analysis.

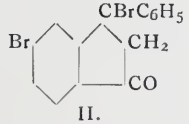
0·1834 grm. substance gave 0·3334 grm. CO_2 and 0·0409 grm. H_2O.

	Calculated for $C_{15}H_{10}OBr$.	Found.
C	49·18	49·57
H	2·70	2·47

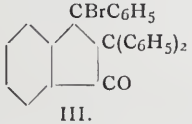
The substance is isomeric with the product melting at 143°, and when oxidised with potassium permanganate it likewise gives brombenzoylbenzoic acid. The two are therefore either stereoisomers due to the presence of two unequal asymmetric carbon atoms or structural isomers that differ in the position of the bromine atom in the second ring :—



I.



II.



III.

Only substances related in this way could be formed in the reaction with brombenzene, and also give *p*-brom-*o*-benzoylbenzoic acid on oxidation. Formula II. is, however, exceedingly improbable for either of the substances in question, because, judging from the observations made with the corresponding triphenylindene derivative (III.), the bromine in a compound with this structure would be as reactive as the bromine in triphenylbrommethane. This is not the case. It is much more probable, therefore, that the substances are stereoisomers (I.). This conclusion is supported by the ease with which the higher melting is transformed into the lower melting substance by heating. A perfectly clean and almost complete transformation is obtained by keeping it at its melting-point for an hour.

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,*

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, &c.

By PERCY H. WALKER.

(Continued from p. 68).

Paints.

Strength Test.

The strength of pigments does not bear a very close relationship to the chemical composition, hence a quantitative analysis does not necessarily give the information actually desired. For this reason the "strength test" is of great importance. A standard colour is usually selected, but in case no standard is used all of a series of similar colours may be compared with one another.

Weigh equal portions of the samples to be tested, and, if available, a standard sample ; add to each equal portions of pure zinc oxide, the amount depending upon the character of the colour tested (this may vary from 5 to 60 times that of the colour). Rub up each mixture on a glass plate or, better, a stone slab, until there is no change in shade on further rubbing. Rate the samples in the order of their depth of tint. White pigments may be rated in a similar way by grinding up each with the same coloured pigment, such as Venetian red. With yellows use chrome green or Prussian blue instead of a white diluent. Add the same number of drops of raw linseed oil to all samples in grinding for the strength test.

White Pigments.

1. *White Lead.*—Pure white lead is basic carbonate of lead and should approach the following composition : $2PbCO_3Pb(OH)_2$. It should be completely soluble in acetic acid. Test for barium and calcium by the flame test. Use an iron wire, as platinum will be ruined by the lead.

(a) *Total Lead.*—Weigh 1 grm. of the sample, moisten with water, dissolve in acetic acid, filter, and wash, ignite, and weigh the insoluble impurities. To the filtrate from the insoluble matter add 25 cc. of sulphuric acid (1 : 1), evaporate and heat until the acetic acid is driven off ; cool, dilute to 200 cc. with water, allow to stand for two hours, filter on a Gooch crucible, wash with 1 per cent sulphuric acid, ignite, and weigh as lead sulphate. Calculate to total lead ($PbSO_4 \times 0{\cdot}68292 = Pb$), or calculate to basic carbonate of lead (white lead) by multiplying the weight of lead sulphate by 0·85258.

The filtrate from the lead sulphate may be used to test for other metals, though white lead is only rarely adulterated with soluble substances ; test, however, for zinc, which may be present as zinc oxide.

Instead of determining the total lead as sulphate it may be determined as lead chromate by precipitating the hot acetic acid solution with potassium dichromate, filtering on a Gooch crucible, igniting at a low temperature, and weighing as lead chromate.

(b) *Complete Analysis.*—When it is necessary to determine the exact composition of a pure white lead, heat 1 grm. of the pigment in a porcelain boat in a current of dry carbon-dioxide-free air, catching the water in sulphuric acid and calcium chloride and the carbon dioxide in soda lime or potassium hydroxide (1·27 specific gravity). By weighing the residue of lead monoxide in the boat all the factors for determining the total composition are obtained. Figure the carbon dioxide to lead carbonate ($PbCO_3$), calculate the lead monoxide corresponding to the lead carbonate ($PbCO_3$) and subtract from the total lead monoxide, calculate the remaining lead monoxide to lead hydroxide ($Pb(OH)_2$), calculate the water corresponding to lead hydroxide and subtract from the total water, the remainder being figured as moisture.

This method assumes the absence of acetic acid. Thompson (*Journ. Soc. Chem. Ind.*, 1905, xxiv., 487) states that acetic acid varies from 0·05 per cent in Dutch process white lead to 0·7 per cent in some precipitated white leads. It is then more accurate to determine the carbon dioxide by evolution ; this is especially the case when working with a lead extracted from an oil paste, as the lead soap and unextracted oil will cause a considerable error by the ignition method. In determining carbon dioxide by the evolution method, liberate the carbon dioxide with dilute nitric acid, have a reflux condenser next to the evolution flask, and dry the carbon dioxide with calcium chloride before absorbing it in the potassium hydroxide bulbs.

(c) *Acetic Acid.*—It is sometimes necessary to determine acetic acid. The Navy Department specifications demand that white lead shall not contain "acetate in excess of fifteen one-hundredths of 1 per cent of glacial acetic acid." Thompson's method (*Journ. Soc. Chem. Ind.*, 1905, xxiv., 487) is as follows :—

Eighteen grms. of the dry white lead are placed in a 500 cc. flask, this flask being arranged for connection with a steam supply, and also with an ordinary Liebig condenser. To this white lead is added 40 cc. of syrupy phosphoric acid, 18 grms. of zinc dust, and about 50 cc. of water. The flask containing the material is heated directly and distilled down to a small bulk. Then the

* *Bulletin* No. 109, Revised, U.S. Department of Agriculture Bureau of Chemistry.

steam is passed into the flask until it becomes about half full of condensed water, when the steam is shut off and the original flask heated directly and distilled down to the same small bulk—this operation being conducted twice. The distillate is then transferred to a special flask and 1 cc. of syrup phosphoric acid added to ensure a slightly acid condition. The flask is then heated and distilled down to a small bulk—say, 20 cc. Steam is then passed through the flask until it contains about 200 cc. of condensed water, when the steam is shut off and the flask heated directly. These operations of direct distillation and steam distillation are conducted until 10 cc. of the distillate require but a drop of tenth-normal alkali to produce a change in the presence of phenolphthalein. Then the bulk of the distillate is titrated with tenth-normal sodium hydroxide, and the acetic acid calculated. It will be found very convenient in this titration, which amounts in some cases to 600—700 cc., to titrate the distillate when it reaches 200 cc., and so continue titrating every 200 cc. as it distils over.

If the white lead contains appreciable amounts of chlorine it is well to add some silver phosphate to the second distillation flask and not carry the distillation from this flask too far at any time.

The method used by the chemists of the Navy Department is as follows:—Weigh 25 grms. of white lead in an Erlenmeyer flask, add 75 cc. of 25 per cent phosphoric acid, distil with steam to a 500 cc. distillate, add to the distillate some milk of barium carbonate, bring to a boil, filter, keeping the solution at the boiling-point (it is not necessary to wash), add an excess of sulphuric acid to the filtrate and determine the barium sulphate in the usual manner; subtract 53 mgrms. from the weight of the barium sulphate and calculate the remainder as acetic acid ($BaSO_4 \times 0{\cdot}515 = CH_3COOH$). The object of this rather indirect method is to avoid any error that might arise from fatty acids being carried over by the steam distillation. For white lead that has not been ground in oil, Thompson's method is to be preferred.

2. *Lead Zinc Whites.*—French zinc is practically pure zinc oxide, being made from metallic zinc. American zinc is made by roasting zinc ores, and almost always contains some lead. Sublimed lead is made by volatilising galena, and as sphalerite is usually associated with the galena, it nearly always contains zinc oxide in addition to the basic sulphate of lead. Zinc lead is essentially lead sulphate and zinc oxide.

(a) *Moisture.*—Dry 2 grms. for two hours at a temperature of 105° C.

(b) *Soluble Sulphate.*—Boil 1 grm. of the sample with 75 cc. of water and 25 cc. of alcohol, filter, wash with a mixture of alcohol and water (1 : 3), and determine sulphuric acid in the filtrate by the usual method of precipitation with barium chloride. The soluble sulphate may be calculated to zinc sulphate.

(To be continued).

Isomerisation of Oleic Acid by Displacement of the Double Bond.—A. Arnaud and S. Posternak.—Saytzeff thought that by treating iodostearic acid with alcoholic potash he had obtained an isomer of oleic acid, which he called isoleic acid, in which the double bond was displaced one carbon to the right towards the carboxyl. The authors have, however, found that the reaction is much more complicated, four acids being formed, viz.:—Ordinary elaidic acid, $\Delta_{9\cdot10}$; elaidic acid, $\Delta_{8\cdot9}$; oxystearic acid, $C_{18}H_{36}O_3$; and the original oleic acid, $\Delta_{9\cdot10}$. The fixation of a molecule of hydriodic acid by oleic acid and the subsequent removal of it by alcoholic potash induces at least three different reactions:—(1) Transformation of the oleic acid into its stereochemical isomer; (2) displacement of the double bond towards the hydroxyl; (3) replacement of the iodine in the iodostearic acid by a hydroxyl.—*Comptes Rendus*, cl., No. 23.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, July 8th, 1910.

Prof. H. L. Callendar, F.R.S., President, in the Chair.

A paper entitled "*The Radio-balance; a Thermoelectric Balance for the Absolute Measurement of Radiation; with applications to Radium and its Emanation*," was read by the President.

In this apparatus, which was first constructed in 1905, and was briefly described in an article on Radiation contributed to the "Encyclopædia Britannica," heat supplied by radiation is directly compensated by the Peltier absorption of heat in a thermo-junction through which a measured electric current is passed. In the simplest form of the instrument, radiation admitted through a measured aperture, 2 mm. diameter, falls on a small copper disc 3 mm. diameter, by 0·5 mm. thick, to which two thermo-junctions are attached, forming a Peltier cross. One couple is connected to a sensitive galvanometer for indicating changes of temperature. The other is connected to a battery and rheostat in series with a millammeter or potentiometer for measuring the current required to reduce the deflection of the galvanameter to zero. If A is the area of the aperture in sq. cm., Q the intensity of the radiation in watts per sq. cm., a the absorption-coefficient of the surface of the disc, P the Peltier coefficient in volts, C the balancing current in ampères, and R the effective resistance of the couple, the equation giving the value of the radiation in absolute measure is—

$$aAQ = PC - C^2R.$$

The absolute value of P is the product of the absolute temperature by the thermoelectric power. The value of R, in the small correction term for the Joule effect, is readily determined by observing the neutral current, $C_0 = P/R$, for which the Joule effect balances the Peltier effect. In practice two similar discs with similar connections are mounted side by side in a thick copper box, and are balanced against each other in order to avoid changes of zero due to exposure to sunshine, or rapid variations of temperature.

The advantages of the disc radio-balance are that it is very simple to construct and easy to reproduce without material variation in the reduction constants. It is very suitable for measurements of solar radiation, or strong sources, but is insufficiently sensitive for weak sources; and the absorption coefficient a must be determined by comparison with a standard.

In the cup radio-balance, the radiation is received in a copper cup, 3 mm. diameter by 10 mm. deep, so that the absorption coefficient is practically equal to unity. Greater sensitiveness is secured by employing a pile of several couples, insulated from the cup, in place of the single balancing couple. External disturbances are eliminated by employing a pair of cups, similarly mounted but oppositely connected, enclosed in a thick copper cylinder. The Joule effect, represented by the C^2R term in the equation, is automatically eliminated by passing the same current in series through the opposing Peltier junctions soldered to the bottom of the cups. The cup exposed to radiation is cooled, and the cup screened from radiation is heated by the Peltier effect, while both are equally heated by the Joule effect. A complete observation involves reversing the current and switching over the radiation screen, in order to eliminate any difference of sensitiveness of the two piles. By observing the neutral current, each cup can be used separately, as with the disc balance, but the disc balance cannot be used with the Peltier couples connected in opposition, unless the balancing couples are insulated from the discs. The cup radio-balance is sensitive to less than a tenth of a microwatt, and is very suitable for

measuring the heat evolved by small quantities of radio-active substances. It was applied to radium at Prof. Strutt's suggestion, and Prof. Rutherford has very kindly supplied samples of emanation, and has determined the value of the radium sample employed by comparison with his own standards. The second sample of emanation had only just come to hand, and the absolute values had not been finally reduced at the time the paper was read; but it appeared from the preliminary reductions that the heat evolution of radium in terms of Prof. Rutherford's standards was much greater than that given by previous observers.

The instruments exhibited at the meeting included (1) a disc radio-balance equatorially mounted for solar radiation; (2) a laboratory pattern, with water or steam jackets for determining the temperature coefficients, and for investigating the theory of the instrument; (3) a cup radio-balance, with which the heat production of radium and its emanation were demonstrated. The latter instrument is capable of measuring the heat evolved from 1 mgrm. of radium to about 1 part in 1000.

Dr. J. A. Harker expressed his interest in the paper, especially in the details of the construction of the various instruments exhibited.

Mr. A. Campbell asked what were the materials of the wires used for the thermo-couples.

The President, in reply to Mr. Campbell, said he had used iron-constantin couples.

A paper entitled "*The Convection of Heat from a Body cooled by a Stream of Fluid*" was read by Dr. A. Russell.

Attention is directed to certain deductions made by Boussinesq from the mathematical theory of the conduction of heat in liquids. Complete proofs are given of Boussinesq's formulæ, stress being laid on their limitations, and some of their practical applications are pointed out. It is proved that when a hot body is immersed in a stream of liquid flowing with constant velocity, the cooling is proportional to the difference of temperature between the body and the liquid. Newton proved experimentally in 1701 that this law was true for the case of a hot body being cooled by a draught of air. He enunciated his law with reference to the forced convection of heat from a body, and not, as is often stated, to the natural free convection from it. Lorenz has shown that in special cases the natural convection of heat will vary as the 1·25th power of the difference of temperature. Provided that the velocity of the cooling draught is kept constant between certain limits, Compan has shown that Newton's law is very approximately true even when the difference of temperature is as high as 300° C. Another deduction from the formulæ proved in the paper is that the cooling is very approximately proportional to the square root of the velocity of the convection current.

The author gives the solution of the problem of the heating of a liquid flowing steadily, with a velocity less than the critical velocity, through a cylindrical tube which is maintained at constant temperature. It is shown that, in many practical cases, the heating power of the tube varies as $R\theta\sqrt{s\sigma kVl}$, where R is the radius of the tube, θ the difference of temperature between the tube and the liquid, s the specific heat, σ the density, k the conductivity, V the velocity of flow, and l the length of the tube.

It is proved that if a wire be immersed in a stream of liquid with its length at right angles to the direction of flow, the electric current which will fuse the wire varies as the 1·25th power of the diameter of the wire.

Finally, the effect on the cooling of an electrically heated cylinder by a stream of liquid, of putting an insulating wrapping round it, is considered. It is shown that in certain cases the effect of this procedure is to lower the temperature of the cylinder, an effect which can be easily demonstrated experimentally. In order to simplify the mathematical work, only the case of incompressible fluids is considered. Experimental results, however, obtained by various physicists are quoted to show that some of the formulæ are approximately true for the cooling of heated bodies by convection with currents of air.

A paper on "*Hysteresis Loops and Lissajous' Figures, and on the Energy wasted in a Hysteresis Loop*" was read by Prof. S. P. Thompson.

Attempts have been made to find an explanation of the forms of the looped curves which express the hysteresis exhibited by iron and steel when subjected to cycles of magnetisation. Physical explanations to account for their general shape have been given by Ewing and Hopkinson, and M. Pierre Weiss has put forward an electronic theory to account for the principal features. The author shows that any hysteresis loop can be analysed into a harmonic series of closed curves corresponding to the various terms in the analysis of the current wave, and their constituents are examined in the paper. A number of examples of hysteresis loops were chosen and subjected to analysis. The loops chosen related to various kinds of iron and steel, hard and soft, solid and laminated, and taken by various methods. In carrying out the analysis the simple approximate method described by the author (*Proc. Phys. Soc.*, vol. xiv.) was used. Details are given of the analysis of various loops, the effect of eddy currents on the size and form of the loops is discussed, and an account is given of the effect of the higher sine and cosine constituents of the current wave.

Dr. Russell thanked the author for his most interesting and instructive paper. In connection with Dr. Thompson's orthogonal ellipse, he showed how an indefinite number of two-beaked loops similar to the hysteresis loop can be made up by quadrants of ellipses, each loop having the same height, the same area, and the same breadth as the orthogonal ellipse. Two-beaked loops having equal areas, breadths, and heights can also be made up from portions of any two curves provided that these curves are similar. He thought it would be of value to discuss the harmonics of the magnetising current, as deduced from the statical hysteresis loop, when the flux varied according to laws other than the harmonic law. F. J. Dykes had investigated the law according to which the flux must vary in order that the magnetising current may have a pure sine shape. To find the harmonics of the flux curve in this case and compare them with the harmonics of the current curve in the author's case would be of interest. A practical use of Dr. Thompson's rapid method of analysing the current wave into its harmonics is that it enables us to compute approximately the eddy-current losses in iron in certain cases by utilising J. J. Thomson's and Heaviside's formulæ.

Dr. W. H. Eccles, referring to the emphasis laid by Prof. Thompson on the hysteresis ellipse obtained by his ingenious mode of analysis of the hysteresis loop, suggested that other closed curves would be obtained if other normal functions were used in the analysis. In regard to the author's suggestion that his results affected our notions of the phenomenon called hysteresis, he thought no change was needed if we kept the term to its original meaning of a lag in state, in contradistinction to (what is often implied) a lag in time.

A paper entitled "*The Energy Relations of certain Detectors used in Wireless Telegraphy*," by Dr. W. H. Eccles, was taken as read.

The paper is a record of the results of an experimental examination into the physical properties of the electrolytic detector, the zincite rectifier, the carborundum rectifier, and a thermoelectric detector consisting of a light contact between graphite and galena. The conditions of the experiments have been generally identical with those arising in the ordinary employment of the detectors, and, in particular, the quantities of energy given to the instruments, in the form of electrical oscillations, have been of the same order in these experiments as in actual practice. Three ways of investigation are followed. The first way consists in applying to the detector an electromotive force which is gradually increased, and measuring the current

at each step. The second way is to fix the electromotive force at some particular value, to send trains of oscillations of various energy values through the instrument, and to measure the intensity of the sound produced in the telephone on each occasion. The third way is to send trains of constant energy value through the instrument while the steady electromotive applied to it is varied, and to measure at each step the intensity of the sound produced in the telephone. These modes of investigation give curves that may be called respectively the steady current curve, the power curve, and the sensitiveness curve. The chief fact brought to light is that the power curves of all the detectors are straight lines, which suggests that all the detectors are fundamentally thermal in their action.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cl., No. 24, June 13, 1910.

Action of Hydrogen on Carbon Monoxide.—Armand Gautier.—The reduction of carbon monoxide by hydrogen begins at 400°, *i.e.*, well below a red-heat. Some water, carbon dioxide, and a little methane are formed. These reciprocal reactions are limited, and have their optimum at about 1000°. The formation of methane increases with the relative proportion of hydrogen. When carbon monoxide and water vapour are passed through a tube heated to 1300° carbon dioxide is formed. These reactions would explain the occurrence of carbon monoxide, carbon dioxide, hydrogen, water, and methane in volcanic gases, if it were assumed that carbon monoxide and hydrogen or carbon dioxide and hydrogen were present in the depths of the earth.

Formation and Decomposition of Thiols.—Paul Sabatier and A. Mailhe. The thiols can be prepared by the action of sulphuretted hydrogen on vapours of alcohols in contact with anhydrous thorium oxide above 300°. Other metallic oxides are much inferior to thorium oxide as catalysers. Cadmium sulphide readily induces the decomposition of thiols into sulphuretted hydrogen and neutral sulphide according to the equation:— $2C_nH_{2n+1}.SH = H_2S + (C_nH_{2n+1})_2S$. This reaction occurs at a moderate temperature. At a higher temperature the ethylene hydrocarbon is formed: $C_nH_{2n+1}.SH = H_2S + C_nH_{2n}$. Probably an unstable thiolate of cadmium is formed as an intermediate product:

$$CdS + 2(C_nH_{2n+1}.SH) = (C_nH_{2n+1}.S)_2Cd + H_2S$$
$$(C_nH_{2n+1}.S)_2Cd = CdS + (C_nH_{2n+1})_2.S.$$

The secondary thiols have a greater tendency to yield hydrocarbons, but neutral sulphides can be obtained from them.

Double Sulphates of Thorium.—M. Barre.—When the solubility of thorium sulphate in solutions of potassium sulphate of different concentrations is determined, it is found that three double sulphates are formed, viz., $Th(SO_4)_2.K_2SO_4.4H_2O$, $Th(SO_4)_2.2K_2SO_4.2H_2O$, $Th(SO_4)_2.3{\cdot}5K_2SO_4$. With sodium sulphate one compound is obtained, corresponding to the formula $Th(SO_4)_2.Na_2SO_4.6H_2O$. Ammonium sulphate yields three salts:—

$$Th(SO_4)_2.(NH_4)_2SO_4.4H_2O,\ Th(SO_4)_2.2(NH_4)_2SO_4.2H_2O,$$
$$Th(SO_4)_2.3(NH_4)_2SO_4.3H_2O.$$

Liquids obtained by the Action of Air on Coal.—P. Mahler and E. Charon.—In the liquid obtained by allowing air to act on coal at 125° the authors have detected acetic acid and traces of formic acid, acetone, and methyl alcohol. Thus exactly the same products are obtained as when wood is distilled.

1-Methyl-1-Ethanoyl Cyclohexane. — P. J. Tarbouriech. — α-Dimethyl-1-carbinol cyclohexanol, $C_6H_{10}OH—COH=(CH_3)_2$, when dehydrated by the action of certain acids gives a ketonic substance of composition $C_9H_{16}O$ and a hydrocarbon C_9H_{14}. The former on oxidation with permanganate in alkaline solution gives a ketonic acid of formula $C_6H_{10}<\begin{matrix}CO-CO_2H\ (1)\\CH_3\ (1).\end{matrix}$ This acid yields an oxime from which the nitrile $C_7H_{13}CN$ can be obtained, and hence the acid $C_7H_{13}CO_2H$. This acid is $C_6H_{10}<\begin{matrix}CH_3\ (1)\\CO_2H\ (1)\end{matrix}$, and thus in the dehydration of the ditertiary glycol, $C_6H_{10}OH—COH=(CH_3)_2$, one of the methyl groups leaves the hexahydrobenzene nucleus and takes up the (1) position.

New Case of Spontaneous Oxidation with Phosphorescence. — Marcel Delépine.— The chlorosulphocarbonic ethers, $CH_3O.CS.Cl$ and $C_2H_5O.CS.Cl$, become strongly luminescent when they are oxidised in air. On the other hand, compounds containing different groupings, or even possessing the isomeric groups—

$$O:C<\begin{matrix}\\S—\end{matrix}\quad\text{and}\quad C<\begin{matrix}O—\\S—\end{matrix}$$

are not phosphorescent. $CSCl_2$, when oxidised, emits much light. The opaque clouds which are formed instantaneously in air are the products of its spontaneous combustion; they smell of carbon oxychloride and contain much sulphuric acid.

Acidity of Derivatives of Oxalacetic Ether.—H. Gault.—Oxalacetic ether and its derivatives have sufficient acidity to allow of a titration with phenolphthalein, while titration with litmus gives no result. Upon this observation can be based a method of determining molecular weights, or at any rate of ascertaining the number of acid hydrogens in the compounds. The titration can be carried out in alcohol or acetone solution. Back titration is advisable, and a low temperature must be maintained in order to prevent saponification. Of the thirteen substances of which the molecular weights were determined only two gave abnormal results, methyloxalsuccinic ether and monoxaltricarballylic ether, always showing themselves more acid than their constitution would suggest.

MISCELLANEOUS.

The Society for the Development of Experimental Sciences and their Practical Applications. — This Society has been formed in connection with the Imperial Moscow University and the Imperial Moscow Technical School, to advance scientific investigations and discoveries by reporting on them, and by giving monetary and other assistance. Communications should be addressed to the Secretary of the Christopher S. Ledentzoff's Society for the Development of Experimental Sciences, Moscow, Russia.

"Fondation George Montefiore Levi" Prize.—The Montefiore Electrotechnic Institute of Liége desires to make it known that a prize having the above title has been instituted and will be awarded every three years, the first award being in 1911. The value of the prize in 1911 will be 20,000 francs (£800). It will be awarded for the best original work presented upon the scientific advance and on the progress of technical applications of electricity in every field. Popular works and simple compilations will be excluded. Works must be in English or French. The jury will consist of ten electrical engineers, five being Belgian and five from other countries. The latest date for receipt is March 31st, 1911. Further particulars are obtainable from the Secretary, Association des Ingénieurs Electriciens sortis de l'Institut Electrotechnique Montefiore, Rue Saint Giles 31, Liége.

THE CHEMICAL NEWS

Vol. CII., No. 2647.

ON SCANDIUM.*

Part II.

By Sir WILLIAM CROOKES, D.Sc., LL.D., For.Sec.R.S.

(Continued from p. 75).

Scandium Aurochloride,

$3ScCl_3,2AuCl_3,21H_2O$.

Scandium aurochloride is prepared by mixing strong solutions of the component chlorides, and allowing the mixture to evaporate slowly over sulphuric acid in a vacuum desiccator. The double salt separates out in a felt-like mass of yellow needle-shaped crystals, which are very deliquescent. In this state the salt has the composition given above. The composition is unusual, but the analytical results agree very well with it, and I have not succeeded in preparing a salt with different proportions of the chief constituents. The water of crystallisation can be driven off gradually by careful heating.

For analysis the felt-like mass of aurochloride was made as dry as possible by pressing it several times between warm dry filtering paper until the paper was unsoiled.

Analysis.

26·717 gr. of scandium aurochloride, dried by pressure, were heated in an air-bath to 100°, and kept at that temperature for three hours. The aurochloride melted to a clear orange-coloured liquid, solidifying on cooling to a crystalline mass. The loss of weight after liquefaction was found to be 4·350 gr.

After keeping the salt for several days at 100° the liquid gradually becomes solid and crystalline, and in this state is anhydrous. The further loss of weight was 2·672 gr., equal to a total loss of 7·022 gr.

The residue from which the water had been driven was dissolved in hot water acidulated with hydrochloric acid, and sodium bisulphite was added. Gold commenced to separate at once, and on boiling the metal collected in a coherent sponge. It was filtered, washed with dilute acid, and weighed after ignition.

After separating the metallic gold, the filtrate was mixed with excess of ammonia and boiled. The precipitated scandia was filtered, washed, ignited, and weighed. The 26·717 gr. of hydrated aurochloride treated in this manner yielded 7·361 gr. of gold, and 3·862 gr. of scandia, = 2·5009 gr. of scandium.

	Theory.			Experiment.	
3Sc ..	132·30	9·21		9·36	
2Au ..	394·40	27·45		27·55	
15Cl ..	531·90	37·01		36·81	
$13H_2O$..	234·21	16·30	26·33	16·28	26·28
$8H_2O$ ..	144·13	10·03		10·00	
	1436·94	100·00		100·00	

2-Hydrate Scandium Aurochloride,

$3ScCl_3,2AuCl_3,2H_2O$.

During the heating at 100° there were strong indications of an arrest of drying when the salt had been heated for about six days, its weight then being 20·355 gr. The following analysis shows that at this stage the salt was a di-hydrate.

Analysis.

20·355 gr. of di-hydrate scandium aurochloride, when further heated to 100° until it was anhydrous, lost 0·660 gr. of water. The residue, treated as described, gave 7·361 gr. of gold and 3·862 gr. of scandia, = 2·5009 gr. of scandium.

	Theory.		Experiment.
3Sc	132·30	12·09	12·29
2Au	394·40	36·03	36·16
15Cl	531·90	48·59	47·62
$2H_2O$ ..	36·03	3·29	3·73
	1094·63	100·00	100·00

8-Hydrate Scandium Aurochloride,

$3ScCl_3,2AuCl_3,8H_2O$.

Scandium aurochloride with eight molecules of water is obtained by drying in a desiccator over sulphuric acid the 21-hydrate. After about a fortnight's drying the weight, which at first rapidly diminishes, becomes constant.

For analysis the hydrate, dried to a constant weight, was dissolved in water and the gold precipitated by the addition of metallic magnesium, the liquid being well boiled. The filtrate from the gold was mixed with an excess of ammonium chloride, ammonia was added, and the whole boiled. The scandia, which came down free from magnesia, was filtered, washed, dried, and ignited.

Analysis.

19·302 gr. treated as described yielded 6·341 gr. of gold and 3·174 gr. of scandia, = 2·0554 gr. of scandium.

	Theory.			Experiment.
3Sc ..	132·30	11·00		10·65
2Au ..	394·40	32·79		32·85
15Cl ..	531·90	44·23	56·21	56·50
$8H_2O$ ..	144·13	11·98		
	1202·73	100·00		100·00

Anhydrous Scandium Aurochloride,

$3ScCl_3,2AuCl_3$.

The weight of the anhydrous salt obtained by continued drying of 26·717 gr. of the 21-hydrate at 100° was 19·695. This amount of anhydrous scandium aurochloride gave 7·361 gr. of gold and 3·862 gr. of scandia, = 2·5009 gr. of scandium.

	Theory.		Experiment.
3Sc ..	132·30	12·50	12·70
2Au ..	394·40	37·26	37·37
15Cl ..	531·90	50·24	49·93
	1058·60	100·00	100·00

Scandium Platinocyanide,

$Sc_2[Pt(CN)_4]_3+21H_2O$.

Scandium platinocyanide is formed by the metathesis in the cold of scandium sulphate and barium platinocyanide

The barium sulphate filtered off, the clear liquid is evaporated at a moderate temperature. Scandium platinocyanide crystallises out in large monoclinic prisms on a rhombic base, the angles of which are 81° 20′ and 98° 40′. The crystals frequently group themselves in rosettes. They are dichroic, crimson by transmitted light, and a rich metallic green by reflected light. The reflected and transmitted rays are oppositely polarised. The red transmitted ray is extinguished when the short diagonal of the nicol is parallel to the long axis of the crystal, and the reflected green ray is extinguished when the long diagonal of the nicol is parallel to the long axis of the crystal. Light passing along the axis of the crystal is crimson, and not polarised.

* A Paper read before the Royal Society, January 20 and June 2, 1910.

[*June 2nd*, 1910.—I have submitted the metallic green crystals of this salt to the low temperature of liquid air with a view to ascertain what change of colour, if any, accompanies the reduction of temperature. After an exposure for ten minutes in liquid air the green colour becomes paler and more of a yellowish hue, while the transmitted light changes from crimson to deep brown. On removing the platinocyanide from the liquid air the normal colours come back as the salt warms up to the temperature of the laboratory.]

The crystals are soluble in water, forming a colourless solution, and are insoluble or nearly so in absolute alcohol. Boiled in alcohol they dehydrate, turning white but not dissolving. The white dehydrated salt dissolves easily in water, and on evaporation separates out in crystals of the normal appearance.

Analysis.

1. 5·755 gr. of well crystallised and air-dried scandium platinocyanide were dissolved in water and precipitated hot with ammonia. The scandia was filtered off, well washed, dried, ignited, and weighed. It weighed 0·627 gr., = 0·406 gr. of scandium. The filtrate was evaporated to dryness in platinum, and the residual ammonium platinocyanide slowly decomposed by heat and then ignited strongly. The platinum left from the decomposition weighed 2·446 gr.
2. 9·612 gr. of scandium platinocyanide were fused at a a full red heat with potassium bisulphate. Hydrocyanic acid was evolved with much intumescence and separation of platinum, and the mixture finally fused quietly to a clear liquid. The mass was extracted with water containing a little acid, and the platinum filtered off; it weighed 4·028 gr.

   Ammonia in excess was added to the filtrate and the precipitated scandia collected; it weighed 1·132 gr. = 0·733 gr. of scandium.
3. 10·741 gr. of air-dried scandium platinocyanide were kept over sulphuric acid in a desiccator for eighty hours. It lost 2·121 gr. of water. The salt was then put into a hot air-oven and kept at 100° for seventeen hours. It became a good canary-yellow, and was found to have lost an additional 0·1343 gr. The temperature was raised to 160° for ten hours, when an additional 0·644 gr. of water was driven off. The temperature was finally raised to about 180°, when the salt began to decompose. Calculated out, these losses nearly approximate to successive losses of 15, 1, and 4½ molecules of water, with half a molecule still remaining in the salt at 160°, and only driven off as decomposition commences.

	Theory.			Experiment.	
				1.	2.
2Sc ..	88·200	6·47	49·37	7·05	49·53
3Pt ..	585·000	42·90		42·50	
12CN ..	312·120	22·89	50·63	50·45	50·47
$15H_2O$.	270·240	19·82			
$1H_2O$ ..	18·016	1·32			
$4\frac{1}{2}H_2O$.	81·072	5·94			
$\frac{1}{2}H_2O$ ..	9·008	0·66			
	1363·656	100·00	100·00	100·00	100·00

	Theory.	Experiment.
		3.
$Sc_2[Pt(CN)_4]_3$ ..	72·26	72·26
$15H_2O$	19·82	19·75
$1H_2O$	1·32	1·25
$4\frac{1}{2}H_2O$	5·94	5·99
$\frac{1}{2}H_2O$	0·66	0·75
	100·00	100·00

Normal scandium platinocyanide is not quite stable when its solution is heated and evaporated. During recrystallisation the solution, at first clear and colourless, deposits a yellow powder, and gives an odour of hydrocyanic acid. Analyses of the yellow deposit have not yet given me concordant results; roughly, it contains 23·5 per cent of scandium and 6 per cent of platinum. The analytical results with the normal platinocyanide given above show an excess of scandium and a deficit of platinum. This may be the result of slight decomposition during re-crystallisation, with production of a trace of the yellow compound.

Scandium Mono-chloroacetate.

$(CH_2ClCOO)_2ScOH + 2H_2O$.

Scandium hydroxide, ground and well shaken with a cold aqueous solution of monochloracetic acid, dissolves slowly and almost completely. The clear filtered solution, evaporated in the cold over sulphuric acid, deposits a crystalline crust, appearing under the microscope as flower-like groups of stellate crystals, and showing good colour when examined by polarised light. These crystals are permanent in dry air, and lose no water at 100°. On being heated they decompose quietly, and at a red heat leave a white residue of scandia.

Analysis.

1. 9·003 gr. of scandium mono-chloroacetate left on ignition 2·193 gr. of scandia, = 1·4202 gr. of scandium.
2. 15·145 gr. of mono-chloroacetate left on ignition 3·634 gr. of scandia, = 2·3530 gr. of scandium.
3. 14·099 gr. of mono-chloroacetate left on ignition 3·387 gr. of scandia, = 2·1934 gr. of scandium.

	Theory.			Experiment.		
				1.	2.	3.
Sc ..	44·10		15·52	15·77	15·54	15·55
C_4 ..	48·00					
H_5 ..	5·04					
Cl_2 ..	70·92	239·99	84·48	84·23	84·46	84·45
O_5 ..	80·00					
$2H_2O$	36·03					
	284·09		100·00	100·00	100·00	100·00

The scandia from these analyses showed when spectrographed no trace of extraneous lines. The earth from the filtrate showed a little yttrium and ytterbium.

Scandium Lactate,

$$\left(\begin{array}{l} CH_3 \\ | \\ CHOH \\ | \\ COO \end{array}\right)_3 Sc + 6H_2O.$$

On mixing hot solutions of scandium nitrate and ammonium lactate, the scandium salt on cooling separates in white feathery crystals, slightly soluble in cold, and more soluble in hot water. It is easily soluble in ammonia; on evaporating the ammoniacal solution crystals are deposited which are double refracting, showing colours in polarised light. Dried over sulphuric acid the crystals of scandium lactate contain six molecules of water, four of which are driven off at 110°.

Analysis.

1. 4·571 gr. of the 6-hydrate scandium lactate left on ignition 0·747 gr. of scandia, = 0·4837 gr. of scandium.
2. 3·379 gr. of the 6-hydrate scandium lactate left on ignition 0·561 gr. of scandia, = 0·3633 gr. of scandium.

	Theory.			Experiment.	
				1.	2.
Sc	44·10		10·52	10·58	10·75
$C_9H_{15}O_9$	267·12		89·48	89·42	89·25
$6H_2O$ ..	108·10				
	419·32		100·00	100·00	100·00

3·863 gr. of scandium lactate, dried at 120°, left on ignition 0·747 gr. of scandia, = 0·4837 gr. of scandium.

	Theory.		Experiment.
Sc	44·10	12·70	12·52
$C_9H_{15}O_9$ ..	267·12	87·30	87·48
$2H_2O$ ..	36·03		
	347·25	100·00	100·00

The scandium nitrate used in the preparation of the lactate contained traces of yttrium and ytterbium. The scandia resulting from the ignition of the lactate showed no appreciable diminution in the amount of impurity present. The mother-liquors, however, appeared free from both yttrium and ytterbium. The impurities in the lactate could only de detected spectroscopically, and were not present in sufficient quantities to interfere with the properties of the lactate, or to increase perceptibly the atomic weight of the scandium.

Scandium Malonate,

$$CH_2<\begin{matrix}COO\\COO\end{matrix}>Sc(OH).$$

Scandium hydroxide dissolves readily in a cold aqueous solution of malonic acid, and the solution when heated deposits a semi-transparent granular precipitate, having no crystalline appearance under the microscope. This precipitate partially dissolves on cooling.

If this solution is boiled for some time a dense precipitate is formed, which on cooling does not re-dissolve.

When a cold solution of scandium malonate containing excess of malonic acid is slowly heated on a water-bath, it becomes cloudy at first; as the temperature rises the liquid becomes clear, and a thick transparent gummy liquid sinks to the bottom. If now the supernatant liquor is poured off and cold water poured on, the transparent colloid-looking mass is slowly converted into a fine white crystalline powder.

The colloidal gummy mass, smeared on a microscopic slide, dries to a clear non-deliquescent glass-like substance. Exposed to dry air the film cracks and flakes off like a pharmaceutical scale preparation.

A lump of the viscid transparent mass, free from adhering water, dried in a water-oven at 100°, becomes white, hard, and brittle. It is now insoluble in either hot or cold water, although before heating the gummy mass is easily soluble in cold water.

The side of the beaker in which the gummy mass is precipitated by heat from the solution of the malonate is seen to be studded with brilliant colourless transparent crystals, some measuring more than a millimetre across.

According to the mode of preparation, scandium malonate contains either one or two molecules of water.

Di-hydrate Scandium Malonate,

$$CH_2<\begin{matrix}COO\\COO\end{matrix}>Sc(OH)+2H_2O.$$

1. 35·331 gr. of di-hydrate scandium malonate left after ignition 12·282 gr. of scandia., = 7·9535 gr. of scandium.
2. 52·299 gr. of scandium malonate, dried at 120°, lost 9·538 gr. of water.

	Theory.		Experiment.	
			1.	2.
Sc	44·100	22·14	22·51	81·76
$C_3H_3O_5$..	119·024	59·77	77·49	
$2H_2O$ ..	36·032	18·09		18·24
	199·156	100·00	100·00	100·00

Mono-hydrate Scandium Malonate.

$$CH_2<\begin{matrix}COO\\COO\end{matrix}>Sc(OH)+H_2O.$$

Analysis.

1. 8·039 gr. of scandium malonate left on ignition 2·984 gr. of scandia, = 1·9324 gr. of scandium.
2. 7·876 gr. of scandium malonate left on ignition 2·958 gr. of scandia, = 1·9155 gr. of scandium.
3. 28·281 gr. of scandium malonate left on ignition 10·537 gr. of scandia, = 6·8235 gr. of scandium.

	Theory.		Experiment.		
			1.	2.	3.
Sc	44·100	24·35	24·04	24·32	24·13
$C_3H_3O_5$ ..	119·024	75·65	75·96	75·68	75·87
H_2O	18·016				
	181·140	100·00	100·00	100·00	100·00

Basic Scandium Malonate,

$$CH_2<\begin{matrix}COOSc(OH)_2\\COOSc(OH)_2\end{matrix}.$$

When a large excess of scandium hydroxide is gently warmed with an amount of malonic acid insufficient to dissolve it, and the filtered solution is well boiled, a basic salt is precipitated having the above composition.

Analysis.

16·754 gr. of the salt left on ignition 8·834gr. of scandia, = 5·7207 gr. of scandium.

	Theory.		Experiment.
Sc_2	88·200	34·15	34·15
$C_3H_6O_8$ ..	170·048	65·85	65·85
	258·248	100·00	100·00

(To be continued).

LUTECIUM AND NEO-YTTERBIUM OR CASSIOPEIUM AND ALDEBARANIUM.

REPLY TO AUER VON WELSBACH'S ARTICLE, "THE DECOMPOSITION OF YTTERBIUM."*

By G. URBAIN.

SINCE 1896 I have devoted myself to the study of the ytterbium earths. By means of long fractional crystallisations, which I applied to all the elements of this group, I have been enabled to isolate systematically europium, gadolinium, terbium, dysprosium, and ytterbium.

After successfully working out this process, which I described in detail in the *Journal de Chimique Physique* ("Recherches sur les Terres Rares," 2ième Mémoire, iv., pp. 31—66, Feb. 26, 1906), I continued the fractionations in order to assure myself of the constancy of the spectral properties and of the atomic weights of the substances after their properties showed that they were pure. When I had settled the questions in the case of europium, gadolinium, terbium, and dysprosium I turned to ytterbium.

In 1905 I had prepared ytterbium nitrate (*Bull. Soc. Chim.*, 1905, xxxiii., p. 739, May 26). The crystallisations were continued on into the year 1907, and then I had no longer enough substance to go on with the fractionation. I published the principal results of these investigations of the elementary nature of ytterbium in a note on November 4, 1907, in the *Comptes Rendus* ("Un Nouvel Elément: Le Lutécium, résultant du Dédoublement de l'Ytterbium de Marignac," *Comptes Rendus*, Nov. 4, 1907; CHEMICAL NEWS, xcvi., 271). I stated in this article that the atomic weight of the ytterbium obtained by me was not constant,

* *Monatshefte für Chemie*, xxx., p. 695. Submitted to the meeting on October 14, 1909. See CHEMICAL NEWS, vol. cii, p. 37.

but varied from 170 to 174. It is true that the fractions which had a lower atomic weight contained a small amount of thulium, but the comparison of the spectra of the different fractions showed very distinctly that Marignac's ytterbium had been split up. I investigated three different kinds of spectra - arc spectra, condensed spark spectra, and uncondensed spark spectra. As regards the first two the investigation extended to the ultra-violet region, and with the last to the visible region. These three methods enabled me, on the ground of the wave-lengths, to characterise distinctly two constituents of ytterbium.

Before this article no properties of these elements were known, and hence the elements themselves were undiscovered. The constituent which was present in smaller quantity and which had the higher atomic weight, I called lutecium; the residue of the old ytterbium I called neo-ytterbium. By this means I reserved to Marignac the honour of his fundamental discovery.

Auer von Welsbach, in continuation of his earlier researches, was at the same time seeking for the elementary constituents of ytterbium. In 1905 (*Anzeiger der Mathematisch - Naturwissenschaftlichen Klasse de Kaiserl. Akademie der Wissenschaften in Wien*, 1905, No. 10) he stated that he was practically convinced of the complexity of this element, but he gave no specific characteristics of its constituents—not even a wave-length.

In 1906 (*Situngsberichte der Mathematisch-Naturwissenschaftlichen Klasse der Kaiserl. Akademie der Wissenschaften*, 1906, II. B, vol. cxv., p. 737) he published a very categorical article, in which he pointed out that he had succeeded in separating the constituents of ytterbium, but he did not characterise them further. He published an article on this subject in 1907 (*Liebig's Ann.*, 1907, vol. cccli., p. 464). But on December 19, 1907, *i.e.*, forty-four days after the meeting of the Académie des Sciences de Paris, when I made my announcement, thirty-seven days after the publication of the report of the meeting and thirty-five days after it might be assumed that this report was received in Vienna, Auer v. Welsbach finally decided to make a report to his colleagues of the Akademie der Wissenschaften in Wien on the constituents of ytterbium as they appeared from his research.

These results were partly given in Protocol No. 27 of the *Sitzungs. der Mathematisch-Naturwissenschaftlichen Klasse der Kaiserl. Akademie in Wien* of Dec. 19, 1907 (*Anzeiger*, 1907, p. 488), which was published long before the appearance of the *Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Klasse* (vol. cxvi., II. B), which contained Auer v. Welsbach's final experiments and which appeared first in May, 1908. (Also to be found in the *Monatsheft für Chemie* in February, when the date of publication is given as March 21, 1908).

As I learnt from the protocol of the meeting of December 19, 1907 (*Anzeiger der Mathematisch - Naturwissenschaftlichen Klasse*, 1907, No. 27, p. 488) that Auer v. Welsbach gave the names cassiopeium and aldebaranium to the elements which have the atomic weights 174·54 and 172·90 respectively, I concluded that they could only be lutecium and neo-ytterbium, and then I laid before the Académie des Sciences de Paris on February 24, 1908, a second note to supplement the first.

Among other information I gave in full the series of numbers which I had obtained in the atomic weight determinations. When I quoted the protocol of December 19, 1907, I pointed out that, judging from the atomic weights, aldebaranium and cassiopeium were identical with lutecium and neo-ytterbium. Then I said:—"It is true that Auer v. Welsbach and I, independently of one another, have studied the same question for some years, as I have already stated in my first note; it is not less true that I was the first to give numerical results, both of atomic weight determinations and of spectral measurements, to characterise the new elements. As Auer von Welsbach's communication only confirms researches previously published, which he was not in a position to do before, there can be no question of new names for lutecium and neo-ytterbium, which have already been named." This obviously referred only to the protocol which was published before my second note. The final account of the work of Auer v. Welsbach first appeared in May, 1908, or in March if the date of the appearance of the *Monatsheft* is taken as basis (*Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Klasse*, vol. cxvi., II. B). This must not be confused with the protocol of the *Sitzungs. der Akademie der Wissenschaften in Wien* of December 19, 1907, which was published long before.

This communication contained a new description—but much more detailed than mine—of lutecium and neo-ytterbium under the names cassiopeium and aldebaranium. In it for the first time Auer v. Welsbach gave numerical results and spectral properties, to which he had previously only made indefinite allusions, which were much too vague to base actual priority upon.

Of thirty-four spectral bands which I had ascribed to lutecium thirty were to be found in the spectra described as belonging to cassiopeium.

While I had given 174 as the limiting atomic weight of lutecium, Auer v. Welsbach ascribed the atomic weight 174·23 to cassiopeium. Thus there could be no doubt that cassiopeium was identical with lutecium and aldebaranium with neo-ytterbium.

Although in this communication Auer v. Welsbach did not quote my note of November 4, 1907, he made an allusion to it, to which I replied in an article which appeared on the front page of the *Chemiker Zeitung* (1908, No. 62).

In the report for the year 1909 the International Atomic Weight Commission—of which I am a member—adopted my nomenclature, regarding my priority as proved.

After Auer v. Welsbach had left the first of these publications (G. Urbain, "Zur Zerlegung des Ytterbiums in seine Komponenten Neo-ytterbium und Lutecium oder Aldebaranium und Cassiopeium, *Chemiker Zeitung*, 1908, No. 62) unanswered for a long time, and had let the second (F. W. Clarke, W. Ostwald, T. E. Thorpe, and G. Urbain, "Rapport du Comité International des poids Atomiques pour 1909) pass without protest, he finally laid his article "Zur Zerlegung des Ytterbiums" before the meeting of the Akademie der Wissenschaften in Wien on October 14, 1909—an article which was published in January, 1910.

In this article Auer v. Welsbach alludes to the articles which he had published on the complexity of ytterbium before my note of November 4, 1907, had appeared, and in it is defined the actual point at issue in this question of priority. Auer v. Welsbach has reproduced these documents in his article *in extenso*. It can thus easily be established that he was not before me in characterising the components of the old ytterbium, and this is exactly what I said in my article of November 4, 1907.

As there is no more to be said about this fact, Auer v. Welsbach has tried to change the ground of the argument.

He could not possibly claim the honour of having been the first to prove the composite nature of ytterbium. The first document (*Anzeiger der Mathematisch-Naturwissenschaftlichen Klasse der Kaiserl. Akademie der Wissenschaften in Wien*, 1905, No. 10), which Auer v. Welsbach quotes at the end of his article, mentions that Exner and Haschek in 1899 had already advanced arguments with regard to the complexity of Marignac's element. These arguments (Exner and Haschek, "Uber die ultra-violetten Funkenspektren der Elemente, xvii., Mitteilung," *Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Klasse der Kaiserl. Akademie der Wissenschaften*, 1899, cviii., II. A, p. 1143) are, as regards spectral properties, incomparably more definite than those which Auer v. Welsbach put forward later. But it is clear that Auer v. Welsbach attributes no real value to this priority, for he ascribes the honour of the discovery not to these two authors, but to himself.

Auer v. Welsbach now tries to prove that he was the first to decompose ytterbium into its components. But as

he gives no cogent proof of this, and it was I who stated the specific properties of the new elements, he entrenches himself behind the verbal statements which he says he or his assistants would have made to anyone who was so indiscreet as to ask him for numerical results before he had published them in his official notice to the Akademie der Wissenschaften in Wien (*Sitzungsberichte der Mathematische - Naturwisscuschaftlichen Klasse der Kaiserl. Akademie der Wissenschaften in Wien*, 1906, cxv., II. B, p. 737). The criticism of my work which Auer v. Welsbach puts forward has nothing to do with the question of priority. It relates only to minor points, as there is no doubt of the identity of his substances with mine.

Thus there remains of Auer v. Welsbach's article nothing more than remarks from which I am with difficulty forced to understand that he goes so far as to charge me with copying his results.

I cannot answer such a charge until it is more definitely stated. And it would really be unworthy of Auer v. Welsbach to make such a charge against a colleague, and, moreover, in an ambiguous form. It would also be beneath me to read into Auer v. Welsbach's statements a meaning which possibly he did not intend to convey.

However, it might easily be a misconception, as the following quotation shows:—"I may mention that in his second publication which was sent in February, 1908, to the Académie in Paris, in speaking of my article mentioned above, which was not issued till May, 1908, he unfortunately gave my atomic weights partially incorrectly, and also affirmed that I had contented myself with saying that differences in their spectra (the ytterbium elements) existed, without further defining them."

I have before me the protocols of the meetings of the Akademie der Wissenschaften in Wien (*Sitzungsberichte der Mathematisch - Naturwissenschaftlichen Klasse*, December 19, 1907), as I had when I quoted them in my February note. I find there no wave-lengths of the new elements, but I see the statement of the atomic weights which I quoted, omitting the second decimal place.

If Auer v. Welsbach complains that these numbers are not exact, it is not I who am answerable.

In the first publications we find Cp = 174·54 and in the second 174·23. This last number was the mean of three numbers, the highest of which was 174·25.

This protocol (*Sitzungs. der Mathematische-Naturwissensehaftlichen Klasse*, December 19, 1907) is not found among the documents which appear as an appendix to Auer v. Welsbach's article, and yet it is of the greatest importance in estimating the value of Auer v. Welsbach's claims.

I cannot suppose that Auer v. Welsbach intentionally did not quote this protocol, and yet it is difficult to believe that he, as a member of the Akademie der Wissenschaften in Wien, did not know that this Akademie publishes their protocols *in extenso* (*Sitzungs. der Mathematische-Naturwissenschaftlichen Klasse*) long before the appearance of the original articles, which are read at their meetings and which are then printed in the *Sitzungsberichte* or in the *Monatshefte für Chemie*.

It is now Auer v. Welsbach's turn to explain whether he wishes me to follow up this point, as, apart from these last doubts, my priority cannot be questioned.

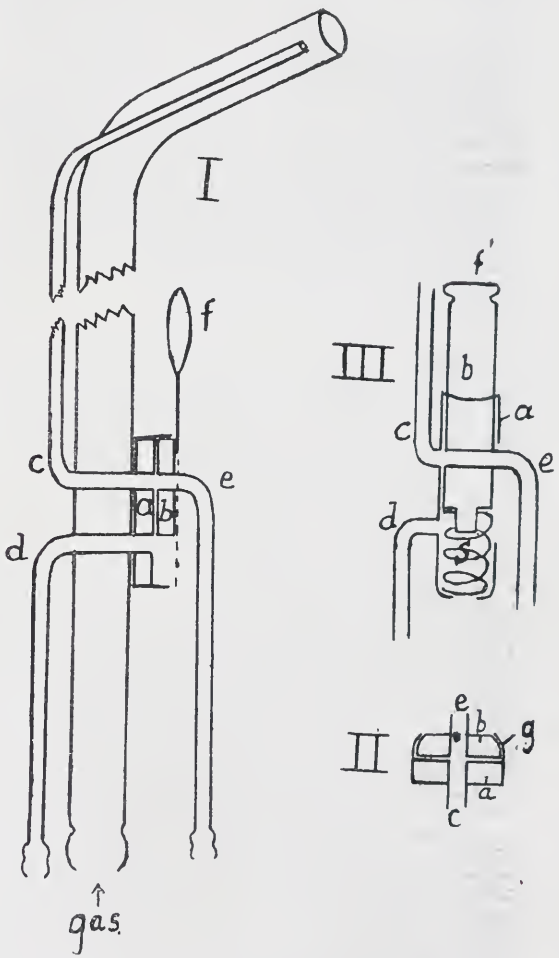
"Allen's Commercial Organic Analysis."—Messrs. J. and A. Churchill have a new edition of Vol. III. of this work just ready for publication. This volume has been re-written under the editorship of Mr. W. A. Davis, B.Sc., and Mr. S. S. Sadtler, S.B. The subjects and authors are as follows:—Hydrocarbons, by F. C. Garrett; Naphthalene and its Derivatives, Phthalic Acid, and the Phthaleins, by W. A. Davis; Bitumens, Anthracene and its Associates, Phenols, by S. S. Sadtler; Aromatic Acids, by E. Horton; Gallic Acid and its Allies, by W. P. Dreaper; Modern Explosives, by A. Marshall. It will be seen that each subject is handled by an expert in his department.

AN IMPROVED MOUTH BLOWPIPE.

By L. S. BAGSTER, B.Sc.

In view of the fact that sealed glass joints are now largely used in place of rubber connections for glass apparatus, the following improved mouth blowpipe may be found useful by those who make such joints:—

Ordinarily, for such work one uses a small portable blowpipe similar in type to an ordinary oxy-hydrogen blowpipe, connected to a coal-gas supply by rubber tubing, the air supply being obtained by blowing through another piece of tubing with the mouth. When using such a blowpipe, one hand is occupied in holding the instrument, and, owing to



the necessity for blowing into a glass joint after heating, either the other hand is occupied in changing the tubes in the mouth which lead to the blowpipe and the joint, or the help of another person is necessary.

The improvement consists essentially of a sliding two-way tap attached to the blowpipe, the sliding portion of which can be worked with one finger. By this means one can direct the air supply either to the flame or to the joint with one and the same tube in the mouth. The construction can be seen from the figures. Fig. 1 shows a simple form which is easy to construct.

Two flat pieces of brass, *a* and *b*, held together by a bevel and guides of sheet brass, *g*, have the faces in contact ground together with fine emery powder. (Fig. 2 shows

an end view). The sliding piece, *b*, has one tube, *e*, attached, to which is fixed the rubber tube going to the mouth for the air supply. The tubes *c*, *d*, and *e* are so arranged that by sliding *b* by means of the ring *f*, the air supply *e* may be connected either to the blowpipe through *c* or to the joint through *d*. Stops are fixed to the ends of *a* to prevent *b* being pulled too far. It is easy to keep the ground faces in contact and yet allow them to slide freely, by slightly bending the guides, *g*.

Fig. 3 shows a more convenient form although it is more difficult to construct. The letters correspond to Fig. 1. Instead of a flat slide a cylindrical one is used, working in a piece of brass tubing. The slide should be turned in a lathe to fit. The tube *e* is kept opposite to *c* by means of a spring, *s*. Connection is made with *d* by pressing the handle, *f'*. A slot is cut in the containing tube *a*, through which *e* passes, being screwed into *b* when in position. This serves to retain the slide in its correct position.

With either form it is necessary to have *b* of such a length that, when *e* is opposite to *c* and the glass is being heated, *d* is open to the air and not closed by the end of the slide. Otherwise the air imprisoned will expand on heating, and will blow a hole in the glass when it softens.

It may be found convenient to have the air-tube of the blowpipe fairly large, and to insert a small glass jet, as is customary in many blowpipes, by means of a forceps.

My thanks are due to Mr. C. Cederholm for suggesting and making some mechanical improvements.

Chemistry School, University of Melbourne,
June 23, 1910.

A SIMPLE AND CONVENIENT APPARATUS FOR THE DETERMINATION OF EQUIVALENTS OF METALS AND THE ESTIMATION OF CARBON DIOXIDE BOTH DIRECTLY AND INDIRECTLY.

By MANINDRA NATH BANERJEE,
Lecturer in Chemistry, Bengal National College and School.

I. *Description of Apparatus* (as per diagram).

1. A small flask fitted up with a cork through which three small holes have been bored; into one passes the bulb-tube A, which contains concentrated sulphuric acid, to a little below the neck of the second bulb; into another passes a delivery tube C bent at right-angles, one end of which just comes down the cork within the flask; into the third a small funnel B with two stoppers passes with its end about a centimetre below the cork. The funnel contains a liquid to act upon the substance, which is placed at the bottom of the flask, a rubber tubing D joins the ends of A and C together. The flask with its arrangements (when empty) should not weigh more than 50 grms.

2. A small U-tube, one limb of which is filled with soda-lime to absorb carbon dioxide. This is used in the estimation of CO_2 directly. The other limb is filled with calcium chloride, to absorb any moisture that may come out of soda-lime during absorption of CO_2. One end of this is plugged with cork, or better with glass-rod and rubber tubing; the other is plugged with cotton-wool, which may be removed during its use.

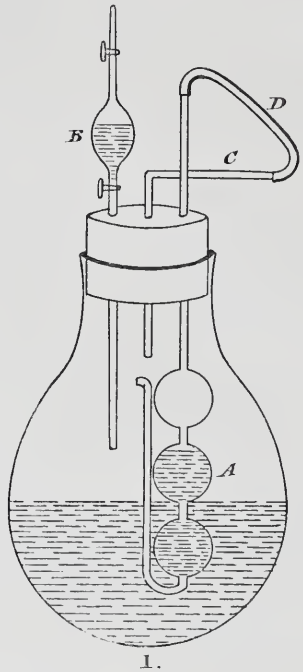
3. A calcium chloride tube containing calcium chloride and soda-lime. This is used to prevent the entering into the flask of any carbon dioxide and moisture when air is blown through, to drive out the least trace of residual gas.

4. A pair of hand-bellows.

5. A calcium chloride tube filled with anhydrous copper sulphate and pumice, and calcium chloride to absorb any hydrochloric acid and moisture that may come out of the apparatus.

II. *Description of Experiment.*

The flask with concentrated sulphuric acid in the bulb-tube A, the reacting liquid in the funnel B to act upon the substance to be placed within, and the rubber tubing D closing the ends of C and A, is carefully weighed. The sulphuric acid is introduced in A by sucking through the rubber tubing attached to the longer end and dipping the other bent end into a watch-glass containing the acid. The reacting liquid is similarly drawn into the funnel B. In certain cases a few cubic centimetres of distilled water are also introduced within and the apparatus weighed along with it.



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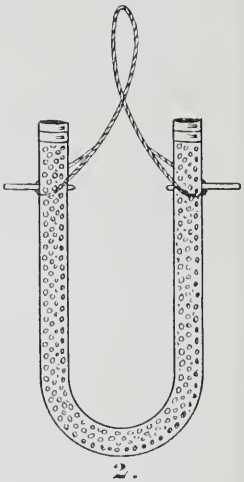
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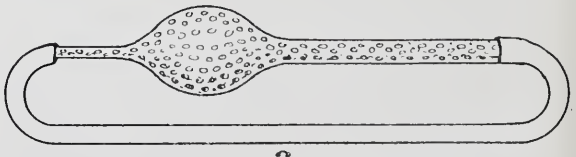
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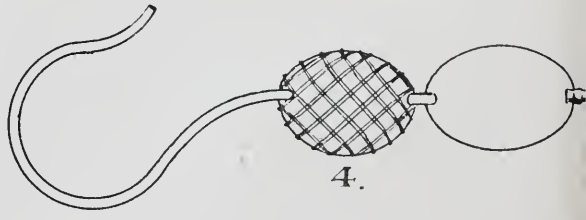
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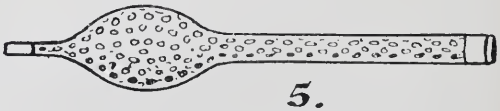
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Next, a small quantity of the substance to be acted upon is placed within the flask, taking care that a bit of it does not stick to the neck of the flask. The cork is carefully inserted, the apparatus wiped clean, and then placed on the pan of the balance. The extra weights required to counterpoise the apparatus give the weight of the substance. If the substance be a metal then a definite quantity of it may be weighed accurately on a watch-glass or weighing-tube

Metal.	Reacting liquid.	Weight of the metal taken.	Equivalent obtained (mean of several observations).	Minimum error. Per cent.	Maximum error. Per cent.
Mg ..	Moderately strong sulphuric acid	0·122 grm.	12·18	0·98	1·6 (*a*)
Zn ..	Moderately strong sulphuric acid	0·05 grm.	33·26	1·18	1·8 (*a*)
Al ..	Saturated solution of caustic potash.	0·1 grm.	9·07	0·6	2·1
Na ..	Moderately dilute sulphuric acid	Weight of sodium amalgam taken, 5·163 grms.; weight of Hg after experiment, 3·992 grms.; weight of Na, 1·171 grms.	22·69	1·56	2·89 (*b*)

(*a*) A little water is placed in the flask before placing the metal.
(*b*) In this experiment sodium amalgam was used. Hence the mercury left in the apparatus was carefully dried and weighed in order to find out the weight of sodium.

and then placed within the flask. The weight of the substances is then noted down.

The apparatus is then placed on the table, better on a piece of white paper or a ground-glass plate. The rubber tubing D is taken off, closing the end C with the thumb. The reacting liquid is allowed to fall from the funnel B very slowly, drop by drop, so as to ensure the regular production of the gas out of the substance, which passes through the bent end, within the flask, of the bulb-tube A; there being no other outlet, it dries out by regular bubbling through the concentrated sulphuric acid placed in the bulbs, and then goes out either to the atmosphere or is allowed to absorb, as in the direct estimation of CO_2 through the calcium chloride tube containing anhydrous copper sulphate and pumice in the weighed absorption U-tube containing soda-lime (*vide* diagram). When all the gas liberated has passed off by regularly bubbling through the sulphuric acid and the substance has been fully acted upon, the ends of A and C are again quickly closed by the tubing D, and the apparatus allowed to remain for a minute, when the next arrangement for blowing off the remaining portion of the gas within the flask is to be made. The absorption tube, if used, should be closed at its open end after the last trace of residual gas is driven off with a plug of rubber tubing and glass rod and allowed to remain cool, after which it is to be weighed again.

For the operation of driving out the last trace of residual gas, take off one end of the rubber tubing attached to the calcium chloride tube (Fig. 3), and connect this with the end C of the delivery tube, quickly removing the rubber tubing D; to the other end of the calcium chloride tube fit up the hand bellows. Then so carefully work with the bellows that the residual gas and air escape through the bulb-tube A very regularly, allowing each bubble as it passes through it to be counted. The bellows should be worked for a few minutes in order to drive out the last trace of the residual gas, and to ensure this at least a volume of air five to six times the capacity of the flask is to be blown through, after which the bellows and the calcium chloride tube are taken out; the rubber tubing D is again attached to the ends of A and C, and the whole apparatus allowed to remain cool, after which it is weighed again.

The difference of the two weighings of the apparatus give the loss in weight suffered by it during the reaction, and this loss clearly represents the weight of the gas liberated from the substance. If the gas is absorbed by the U-tube as in CO_2 estimation, the increase in weight of the U-tube represents also directly the weight of the gas obtained from the substance. If the experiment is performed carefully the gain in weight of the absorption tube must be equal to the loss in weight of the apparatus itself (within the limits of a very small percentage of error).

III. *Experiments Performed with this Instrument.*

Direct and Indirect Estimation of CO_2 *in a Carbonate.*—The bulb-tube A is filled with concentrated sulphuric acid up to the second bulb, the funnel B is filled with moderately strong hydrochloric acid; the apparatus is then weighed carefully in a good balance. Dry precipitated calcium carbonate is then introduced very carefully into the apparatus, which is again weighed to ascertain the weight of the carbonate introduced. The U-tube containing soda-lime is also weighed. The apparatus is worked thus:—The rubber tubing D is taken off the delivery tube C, and connected with the calcium chloride tube containing anhydrous copper sulphate and pumice, and calcium chloride (Fig. 5); the other end of the latter is connected to the U-tube containing soda-lime. The thumb is tightly placed to the end C. The hydrochloric acid is allowed to fall from the funnel drop by drop, the action begins, the gas bubbles through the sulphuric acid very regularly, and goes through the calcium chloride tube into the absorption tube, which become heated as the carbon dioxide is absorbed. If there are gas or air-bubbles separating the sulphuric acid column in the bulbs, a little jerk very carefully given brings the acid to its position. The action is continued for some time, till all the carbonate dissolves completely, when the thumb at C is quickly removed, and the end attached to the calcium chloride tube (Fig. 4) fitted with the hand-bellows, which are worked for a few minutes carefully so that bubble after bubble passes through sulphuric acid, very regularly and not briskly, till the residual gas is completely driven off the apparatus into the absorption U-tube (Fig. 2). The apparatus is then detached from the calcium chloride tube and bellows at the one end, and the copper sulphate and absorption tube on the other. The tubing D is then attached to C and A, and the apparatus allowed to cool for a few minutes, and then weighed. The absorption U-tube is plugged and allowed to cool, and weighed. The gain in weight of the absorption U-tube equals the loss in weight of the apparatus. The former gives the weight of the carbon dioxide *directly*, while the latter *indirectly*, one being the check on the other.

Several experiments have been performed with this instrument, and the minimum error has been 0·76 per cent, while the maximum has reached 1·37 per cent.

The same Apparatus may be conveniently Utilised for a Number of Experiments in the Determination of the Equivalents of Metals.—The equivalents of the following metals have been found out by the apparatus:—Mg, Zn, Na, Al.

In these experiments the apparatus is first weighed with concentrated sulphuric acid up to the second bulb in the bulb-tube A, the reacting liquid introduced in the funnel B, and a little water introduced into the flask, except in the case of Na or such metals as are acted upon by water at the ordinary temperature. The metal is then introduced into the apparatus, which is then weighed, and thereby the weight of the metal ascertained. Next, the tubing D is taken off C, the end of which is carefully closed with the thumb, the reacting liquid gradually allowed to pour from the funnel out into the flask; the hydrogen bubbles produced pass very regularly, bubble after bubble, through the sulphuric acid out in the atmosphere. When the action ceases completely the thumb is taken off the end of C, and to it is attached the calcium chloride tube (Fig. 3) fitted up

with the bellows (Fig. 4), which are carefully worked for several minutes to drive the residual gas out of the apparatus, after which the end of the tubing D is again attached to C, the whole apparatus allowed to cool, and then re-weighed. The loss in weight gives the weight of the hydrogen, from which and from the weight of the metal the equivalent is calculated thus :—

$$W' : 1 :: W : E. \quad E = \frac{W}{W'}.$$

W' = weight of hydrogen, obtained in grms., W = weight of the metal in grms.

1 = 1 grm. of hydrogen, E = equivalent.

The accompanying table shows the results of several experiments performed.

(Note.—The apparatus may also be used in finding out the equivalents of those metals which are easily acted upon by dilute acids, &c.; *e.g.*, Fe, Ca, &c.).

May 19, 1910.

SOME VARIATIONS IN THE OFFICIAL METHOD FOR THE DETERMINATION OF VOLATILE MATTER IN COAL.*

By A. C. FIELDNER and J. D. DAVIS.

In view of the proposed revision of the official methods of coal analysis, it may be of interest to present certain experimental data bearing on the present official method for the determination of volatile matter in coal.

These experiments were conducted in the Pittsburg and Washington laboratories of the U.S. Geological Survey, primarily to ascertain the difference in volatile matter produced by using a 20 cm. natural gas flame as compared with the 20 cm. coal-gas flame. After starting the work it was found desirable to investigate the influence of other factors such as gas pressure, type of burner, and surface condition of platinum crucible, *i.e.*, dull grey or polished. In order to eliminate influence of variation in size and shape, three 30-grm. platinum crucibles of practically the same capacity and weight with closely-fitting covers were used in all the experiments, it having been demonstrated by actual trial that each one of the three crucibles gave the same results.

As these crucibles had been regularly used for volatile determinations, both inner and outer surfaces had the dull grey appearance which platinum assumes when heated several times in the natural gas flame. To protect the flame from air currents, the platinum triangle supporting the crucible was enclosed in a cylindrical sheet metal shield, lined with asbestos, 15 cm. long and 7 cm. in diameter, the platinum triangle being placed 3 cm. below the top of the shield; the bottom of the crucible was exactly 8 cm. above the mouth of the burner.

The temperature measurements were taken on a parallel test, using the same crucible with the regular cover replaced by one of nickel; the thermocouple, inserted through a small opening in the cover, was placed 2 mm. above the bottom of the crucible; the opening around the thermocouple leads was closed with a cement of barium sulphate and sodium silicate.

The description of coals tested is given in Table I.

Influence of Change in Gas Pressure.

Coal-gas can be burned efficiently at low pressures, 2 to 3 inches of water being sufficient; natural gas, owing to the much larger proportion of air required, must be supplied to the burner at higher pressure.

Table II. gives results obtained by varying the pressure from 1 to 13 inches of water.

Table I.

Coal No.	Type.	Locality.
1, 2, 3, 10, 11, 12	Semibituminous	Pocahontas, W. Va.
4, 5, 6	Bituminous	Pennsylvania
7	Anthracite	Pennsylvania

Table II.—*Influence of Gas Pressure on Volatile Matter* (Natural gas; Tyrell burner; 20 cm. flame).

Gas pressure in inches of water.	Per cent volatile matter. Coal No. 1.	Coal No. 3.	Coal No. 6.	Maximum temperature. °C.	Kind of flame.
1	15·4	15·8	32·4	760	Yellow tipped
2	15·2	16·7	—	—	—
3	15·4	16·7	32·3	780	Faint yellow tip.
4	16·3	—	32·7	—	—
5	16·7	16·5	32·6	800	Yellow tip just removed
6	17·2	16·7	33·0	—	Long inner cone
8	16·7	—	32·7	—	—
9	—	17·2	—	825	Well defined inner cone
12	17·2	16·9	32·7	—	—
13	17·1	17·1	32·5	845	Sharp, greenish inner cone

Temperature during Volatile Determination on Coal No. 1 with varying Pressures.

Time, in minutes.	Pressure in inches of water. 1. °C.	3. °C.	5. °C.	9. °C.	13. °C.
0·5	180	185	180	220	320
1	450	440	450	480	550
1·5	590	590	605	635	690
2	670	670	710	720	780
2·5	725	740	765	775	825
3	745	760	790	805	840
3·5	750	770	800	815	848
4	755	780	803	820	848
4·5	760	780	803	820	848
5	760	780	802	823	848
6	760	780	800	823	847
7	760	780	800	823	845

The maximum temperature varies from 760 to 845° C. Coal No. 6, a bituminous coal, gives practically the same yield of volatile matter throughout the series. The semi-bituminous coals, Nos. 1 and 3, are more sensitive to variations in temperature, the extremes being nearly 2 per cent. The maximum pressure, 13 inches, was used in all subsequent work with natural gas.

It has frequently been noted by the writers that during the early part of the seven-minute volatile process, the coke swells or puffs up to the lid of the crucible, oftentimes raising it slightly. On comparing such determinations with duplicates that did not swell, they were invariably found to be 1 to 2 per cent lower in volatile matter. This peculiar swelling has been noticed only in the case of semi-bituminous coals. It is more apt to happen at the lower temperatures, and when the coal is kept perfectly level in the bottom of the crucible. The swelling can be prevented by simply tapping the crucible on one side so as to settle the coal in an inclined position across one corner of the bottom of the crucible, thus preventing the formation of a film of fused coal across the crucible. Comparative results are given in Table III.

* Presented by permission of the Director, U S. Geological Survey. From the *Journal of Industrial and Engineering Chemistry*, ii., No. 7.

Table III.—*Variations due to Swelling or Puffing-up of Coke in Crucible.*

	Coke residue in compact lump in bottom of crucible.	Coke residue swelled half-way to cover.	Coke residue swelled up to cover.
Coal No. 1	16·7	16·2	15·3
	17·2	16·8	14·8
	17·1	16·0	15·2
	—	15·5	15·1
	—	15·7	15·7
	—	—	15·6
Average.. ..	17·0	16·0	15·3
Coal No. 2	17·0	15·4	15·4
	16·9		

Influence of Type of Burner.

It is reasonable to expect some lack of uniformity in volatile results where widely different types of Bunsen burners are used. A burner with a large bore will give a larger flame volume, with a correspondingly increased heating effect. Determinations were made with the following types of burners on both natural and coal-gas :—

(*a*) The simple Bunsen burner, bore 9 mm.
(*b*) The Tyrell burner, bore 9 mm. (Eimer and Amend Catalogue, p. 80).
(*c*) The Fletcher, No. 5*g* burner, bore 12 mm. (Eimer and Amend Catalogue, p. 80).

The results are given in Table IV.

Table IV.—*Influence of different Types of Burners.*

Coal No.	Per cent volatile. Fletcher.	Tyrell.	Bunsen.	Difference. Fletcher and Tyrell.	Fletcher and Bunsen.
	(*a*) Natural Gas.				
1	17·2	17·0	15·7	0·2	−1·5
2	17·0	16·8	15·8	−0·2	−1·2
6	32·8	32·6	32·6	−0·2	−0·2
4	31·8	31·3	31·2	−0·5	−0·6
5	31·5	31·5	—	0·0	—
			Average	−0·2	−0·8
Temp. °C.	850	850	790		
	(*b*) Coal-gas, Pittsburg.				
1	17·0	16·7	16·3	−0·3	−0·7
6	33·0	32·3	—	0·7	—
5	31·7	31·4	—	−0·3	—
			Average	−0·4	
Temp. °C.	855	810			
	(*c*) Carburetted Water-gas, Washington.				
1	18·3	—	17·2	—	−1·1
11	18·6	—	17·8	—	−0·8
12	18·0	—	17·7	—	−0·3
10	18·7	—	18·4	—	−0·3
3	18·8	—	18·5	—	−0·3
2	18·2	—	17·6	—	−0·6
			Average		−0·6
Temp. °C.	970				

The Fletcher burner gives slightly higher volatile matter than the Tyrell with practically the same maximum temperature. The larger flame volume of the Fletcher burner, heats up the crucible more rapidly, which increases the gas yield slightly. With the use of natural gas, the maximum temperature of the Bunsen burner is 60° less than either the Fletcher or Tyrell ; this produces a marked difference in volatile matter in the case of the semi-bituminous coals. Evidently a burner like the Fletcher or Tyrell, admitting of both gas and air regulation, is preferable to the simple Bunsen.

Table V.—*Temperature Measurements* (°C.). *Coal No.* 1.

Time, in minutes.	(*a*). Fletcher burner.	Tyrell burner.	Bunsen burner.	(*b*). Tyrell burner.	(*c*). Fletcher burner.
0·5	280	250	250	260	—
1	590	530	580	540	630
1·5	710	670	700	680	—
2	788	780	760	760	910
2·5	830	825	780	810	—
3	845	840	785	835	975
3·5	850	850	785	850	—
4	850	850	785	855	975
4·5	850	850	790	855	—
5	850	850	790	855	970
6	850	850	790	855	970
7	850	850	790	855	970

(*a*) Natural gas at 13 inches water pressure ; 20 cm. flame.
(*b*) Pittsburg coal-gas at 2·5 ins. pressure ; 20 cm. flame.
(*c*) Washington illuminating gas at 2·5 ins. pressure ; 20 cm. flame.

(To be continued).

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,*

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, &c.

By PERCY H. WALKER.

(Continued from p. 82).

Paints.

White Pigments (continued).

(c) *Insoluble and Total Sulphate.* — Treat 1 grm. in a 600 cc. beaker with 10 cc. of water, 10 cc. of strong hydrochloric acid, and 5 grms. of ammonium chloride, heat on a steam-bath in a covered beaker for five minutes, add hot water to make about 400 cc., boil for five minutes, and filter to separate any insoluble material. (A pure colour should be completely dissolved). Wash with hot water, ignite, and weigh the insoluble. To the boiling hot filtrate add slowly, with stirring, 20 cc. of a 10 per cent barium chloride solution ; let stand for two hours on the steam-bath, filter, wash, ignite, and weigh as barium sulphate. Calculate the total sulphate (SO_4), deduct from it the soluble sulphate (SO_4), and figure the remainder as lead sulphate.

(d) *Lead and Zinc.*—(1) *In the Absence of other Metals.* —Dissolve 1 grm. by boiling fifteen minutes with 250 cc. of water and 20 cc. of strong nitric acid, add 5 cc. of sulphuric acid, evaporate, and heat until all of the nitric acid is driven off and copious fumes of sulphuric anhydride begin to come off ; cool, dilute, filter on a Gooch crucible, wash with 1 per cent sulphuric acid, ignite, and weigh as lead sulphate. Deduct from this the lead sulphate obtained from the sulphate determination and figure the remainder to lead monoxide. Evaporate the filtrate from the lead sulphate to 100 cc., cool, add 5 grms. of microcosmic salt dissolved in water, then add ammonium hydroxide until the solution is just neutral (test with litmus-paper). Then add 2 drops of ammonium hydroxide and 1 cc. of acetic acid, stir vigorously, heat on the steam-bath for an hour (the precipitate should assume a crystalline character and settle well at the end of that time), filter on a Gooch crucible, wash with hot water, ignite at first at a very low heat, and finally heat to redness, and weigh as zinc pyrophosphate ($Zn_2P_2O_7$), calculate to zinc oxide ($Zn_2P_2O_7 \times 0{\cdot}53412 = ZnO$). Deduct the zinc oxide present as zinc sulphate and report the remainder as zinc oxide.
(2) *In the Presence of other Metals.*—With a sample con-

* *Bulletin* No. 109, Revised, U.S. Department of Agriculture, Bureau of Chemistry.

taining calcium or magnesium salts the lead should be precipitated as sulphide from hydrochloric acid solution, then dissolved in nitric acid and determined as sulphate. The filtrates from the lead sulphide can be used to determine the zinc. If it is desired to make a gravimetric determination of zinc, boil off the hydrogen sulphide, add a little bromine water to oxidise any trace of iron, then add ammonium hydroxide in excess; only in rare cases will any iron appear here, but if it does, filter, re-dissolve, and re-precipitate. Manganese will be present only very rarely; if present, it can be precipitated by adding bromine and warming. Make the zinc solution acid with acetic acid, heat to a boil, and pass hydrogen sulphide into the hot solution until it is completely saturated (for twenty to thirty minutes). Allow the zinc sulphide to settle for five hours, filter, wash with hydrogen sulphide water, dissolve the zinc sulphide in hot dilute hydrochloric acid, boil off the hydrogen sulphide, and determine the zinc as pyrophosphate as described.

The hydrogen sulphide method is very troublesome on account of the difficulty of filtering and washing zinc sulphide, and when calcium or magnesium is present it is generally better to determine the zinc volumetrically. This is best done by Low's method ("Technical Methods of Ore Analysis," p. 209). In the absence of iron and manganese take the filtrate from the lead sulphide, add ammonium hydroxide until alkaline, then hydrochloric acid until just acid, then add 3 cc. of strong hydrochloric acid, dilute to about 250 cc., and titrate with standard ferrocyanide just as in standardising the solution. When iron and manganese are present follow the method for oxidised ores as described by Low.

(e) *Standardising the Ferrocyanide Solution.*—Prepare a solution of potassium ferrocyanide containing 22 grms. of the crystallised salt to the litre. Standardise this solution as follows:—Weigh carefully about 0·2 grm. of pure zinc and dissolve in 10 cc. of strong hydrochloric acid (sp. gr. 1·20), using a 400 cc. covered beaker. Dilute somewhat, place a bit of litmus-paper in the solution as an indicator, and make faintly alkaline with ammonium hydroxide. Again acidify faintly with hydrochloric acid and then add 3 cc. excess of the strong acid. Dilute now to about 250 cc. and heat nearly to boiling.

Titrate the hot liquid with the ferrocyanide solution as follows:—Pour off about one-third of the zinc solution and set it aside in a beaker. Titrate the remainder by running in a few cubic centimetres at a time until a drop, when tested on a porcelain plate with a drop of a 5 per cent solution of uranium nitrate, shows a brown tinge. Now add the greater part of the reserved portion, and continue the titration more cautiously until the end-point is again passed. Finally, add the last of the reserved portion, and to save rinsing out the beaker, pour a large part of the solution back into it again and then empty it once more.

Finish the titration very carefully, ordinarily by testing after each addition of two drops. Instead of using a single drop of the zinc solution for the test, the reaction is sharper if a quantity equivalent to several drops is taken. If this is done near the end of the titration the amount of zinc lost thereby will be insignificant. A convenient way of making the test is to use a medicine-dropper and place a single drop of the uranium solution in each depression of the test-plate at the outset. By using a glass tube instead of a rod for a stirrer, any desired quantity of the solution can be quickly removed for a test. When the final brown tinge is obtained, note the reading of the burette, and then wait a minute or two and observe if one or more of the preceding tests do not also develop a colour. The end-point is always passed by a test or two and the burette reading must be corrected accordingly. A further correction must also be made for the amount of ferrocyanide required to produce a colour under the same conditions when no zinc is present. This is ordinarily 2 drops. One cubic centimetre of the standard solution will equal about 0·005 grm. of zinc.

3. *Calcium Pigments.*—Whiting is calcium carbonate and is used extensively as an adulterant. Plaster of Paris is dehydrated calcium sulphate and gypsum is the natural hydrated calcium sulphate ($CaSO_4 + 2H_2O$). Besides these a precipitated calcium sulphate is used, especially as a basis upon which to precipitate aniline colours. A microscopic examination is therefore of importance.

Free lime is objectionable and is especially to be looked for in whiting. Boil 2 grms. of the sample for five minutes with 100 cc. of water, and add phenolphthalein. If red colour develops, free lime may be assumed to be present, though the alkaline reaction may possibly be due to hydrates of sodium or potassium.

For quantitative analysis, when such is necessary, boil 1 grm. of the sample with 25 cc. of hydrochloric acid (1 : 1), add 150 cc. of water, boil, filter, wash, ignite, and weigh the insoluble. Precipitate iron and aluminium hydrates from the filtrate with ammonium hydroxide, dissolve in hydrochloric acid and re-precipitate, wash, ignite, and weigh. Unite the filtrates from the iron and alumina precipitation, heat to boiling, add slowly 25 cc. of a boiling solution of ammonium oxalate (the solution should be saturated at room temperature); let stand on the steam-bath for one to two hours, filter, wash free from chlorides (cold water is better for washing than hot water), and determine the calcium by igniting to constant weight in a platinum crucible. A blast lamp is generally recommended for this purpose, but if a platinum triangle is used to support the crucible, from fifteen to thirty minutes' ignition with a good Bunsen burner will convert the oxalate entirely to oxide with less danger of loss than with a blast. If great accuracy is required, it is well to dissolve the calcium oxalate in hydrochloric acid and re-precipitate.

Instead of weighing the calcium as CaO, it may be determined volumetrically by titrating with potassium permanganate as follows: Precipitate as described, and wash free from ammonium oxalate (when free the filtrate will not react for chlorides). Return the moist precipitate to the beaker by washing with a stream of water, remove the small quantity remaining on the paper with hot dilute sulphuric acid, add 20 cc. of sulphuric acid (1 : 1), dilute to 300 cc., heat to about 80° C., and titrate with tenth-normal potassium permanganate (1 cc. = 0·0028 grm. of calcium oxide). Evaporate the filtrate from the calcium oxalate to about 100 cc., make neutral by the addition of hydrochloric acid, if necessary cool in ice-water, add an excess of a solution of sodium ammonium phosphate, stir, allow to stand for fifteen minutes, then add 20 cc. of strong ammonium hydroxide, stir well, allow to stand for two hours, filter in a Gooch, wash with 2 per cent ammonium hydroxide, ignite gently at first and finally to a bright red, and weigh as magnesium pyrophosphate ($Mg_2P_2O_7$).

4. *Barytes.*—Barytes, being one of the cheapest white pigments, is seldom adulterated. It should be white and well ground. A microscopic examination should be made to determine the evenness of grinding, the size and angularity of the particles, and whether they are amorphous or crystalline.

(a) *Moisture.*—Dry 2 grms. of the sample at 105° C. for two hours. The loss in weight represents the moisture.

(b) *Insoluble.*—Boil 1 grm. in hydrochloric acid (1 : 3), evaporate to dryness, moisten with hydrochloric acid, dilute with water, boil, filter, and wash. If a previous qualitative examination has determined the absence of lead and other easily reduced metals, ignite in platinum, weigh, and calculate the total insoluble; this may generally be safely calculated to barium sulphate ($BaSO_4$), but to determine any silica that may be present add hydrofluoric acid and sulphuric acid, evaporate the acids, ignite, and weigh; calculate the loss as silicon dioxide.

(c) *Alumina and Oxides of Iron.*—Add ammonium hydroxide to the filtrate from the total insoluble, boil, filter, wash, ignite, and weigh as oxide of iron and alumina.

(d) *Lime.*—Precipitate with ammonium oxalate from the filtrate from oxide of iron and alumina, filter, wash, ignite, and weigh as calcium oxide or titrate with potassium permanganate.

(e) *Soluble Sulphate.*—Boil 1 grm. with 20 cc. of strong hydrochloric acid, dilute to 200 cc. with hot water, boil, filter, wash, and determine the sulphate in the filtrate by precipitation with barium chloride in the usual manner. Calculate to calcium sulphate. If carbonates are present calculate the remaining calcium oxide to calcium carbonate (whiting); if carbonates are absent calculate the remainder as lime.

(f) *Loss on Ignition.*—Ignite 1 grm. in a platinum crucible. The loss in weight represents water (both free and combined with gypsum and kaolin), carbon dioxide from whiting, and organic matter. Barytes should contain only small amounts of foreign matter, and there should be 95 per cent or more of barium sulphate present.

5. *Lithopone.*—Lithopone should contain about 65 per cent of barium sulphate, the remainder being zinc sulphide with small amounts of zinc oxide and carbonate. This substance is also called ponolith and Beckton white.

(a) *Analysis of Pure Lithopone (Drawe).*—(1) *Moisture.*—Heat 2 grms. of the sample for two hours at 105° C. There should be less than 0·4 per cent of moisture. (2) *Insoluble and Total Zinc.* Take 1 grm. in a 200 cc. beaker, add 10 cc. of strong hydrochloric acid, mix, and add in small portions about a grm. of potassium chlorate; then heat on the water-bath until about half of the liquid is evaporated. Dilute with hot water, add 5 cc. of dilute sulphuric acid (1 : 10), boil, allow to settle, filter, wash, ignite, and weigh the insoluble which will be total barium as barium sulphate, together with any other insoluble. Make a qualitative examination for alumina and silica (not likely to be present). Heat the filtrate from the insoluble to boiling, add sodium carbonate solution, drop by drop, until all of the zinc is precipitated as carbonate, filter on a Gooch, wash, ignite, and weigh as zinc oxide. (3) *Zinc Sulphide.*—Digest 1 grm. with 100 cc. of 1 per cent acetic acid at room temperature for one-half hour, then filter and wash; determine the zinc in the filtrate as in the preceding analysis. The difference between the total zinc oxide and the zinc oxide soluble in acetic acid multiplied by 1·1973 gives the zinc present as sulphide. The zinc soluble in acetic acid may be reported as oxide, though it may be partly carbonate. This scheme of analysis assumes the absence of impurities such as salts of iron, &c., and is the method of P. Drawe (*Zeit. Angew. Chem.*, 1902, xv., 174).

(b) *Analysis of Lithopone in the Presence of Foreign Substances (Copalle).*—Copalle (*Ann. Chim. Anal. Appl.*, 1907, xii., 62) proposes the following method of analysis:—(1) *Soluble Salts.*—Wash 2 grms. with hot water and determine the nature of the soluble salts. (2) *Moisture.*—Determine on 2 grms. the loss in weight on a steam-bath. (3) *Insoluble.*—Oxidise 1 grm. with nitric acid of 40° B. (1·38 specific gravity), at first cold, then hot. Then add hydrochloric acid, evaporate to very small volume, dilute with hot water, filter, ignite the precipitate which represents the barium sulphate corresponding to the total barium. If the insoluble exceeds 66 to 68 per cent it is necessary to prove that the excess is not due to the addition of kaolin. (4) *Total Zinc.*—Determine as oxide by precipitation as carbonate in the filtrate from the insoluble. When more than traces of iron, alumina, or lime are present, it is best to determine the zinc volumetrically. (5) *Sulphide of Zinc.*—Add a slight excess of hydrochloric acid to the filtrate from the zinc carbonate and determine the sulphur by precipitation in the usual manner. This sulphur multiplied by 3·03, or the weight of barium sulphate ($BaSO_4$) multiplied by 0·4603, gives the zinc sulphide. (6) *Oxide of Zinc.*—Multiply the weight of the zinc sulphide by 0·835 to obtain the zinc oxide corresponding to the sulphide. Subtract this from the total zinc oxide and report the remainder as zinc oxide (it may be present as oxide or as carbonate). (7) *Barium Carbonate.*—Digest 2 grms. with boiling dilute hydrochloric acid, dilute with hot water, filter from the insoluble and determine the barium in the filtrate by precipitation with sulphuric acid. The weight of the barium sulphate multiplied by 0·845 gives the barium soluble in the acid calculated as carbonate. (8) *Barium Sulphate.*—Subtract the barium sulphate corresponding to the carbonate from the total barium sulphate.

6. *General Scheme of Analysis for a White Pigment.*—The pigment may contain white-lead, lead sulphate, zinc oxide, baryta, whiting, kaolin, or other silicates, and, in fact, any mixture of white pigments, except lead compounds and zinc sulphide together, as such a mixture has a tendency to blacken.

Dry 2 grms. of the sample for two hours at 105° C. Treat 1 grm. in a beaker with 25 cc. of water and 10 cc. of acetic acid (95 per cent); boil, filter, and wash with water. Pass hydrogen sulphide into the hot filtrate, collect the lead sulphide and zinc sulphide on a filter, wash, dissolve in nitric acid, precipitate, and weigh the lead as sulphate in the usual manner; calculate to white-lead. In the filtrate from the lead sulphate determine the zinc either by the gravimetric or the volumetric method, and calculate to zinc oxide. Test the filtrate from the lead sulphide and the zinc sulphide for barium, calcium, and magnesium, determine in the usual manner, and calculate to carbonates. Transfer the residue from the acetic acid digestion to a beaker, add 10 cc. of water, 10 cc. of strong hydrochloric acid, and 5 grms. of ammonium chloride, heat on a steam-bath for five minutes, dilute with hot water to 400 cc., boil five minutes, filter, wash, ignite, and weigh the insoluble. Make a qualitative test of the insoluble. Precipitate the lead from the filtrate from the insoluble with hydrogen sulphide, dissolve in nitric acid, determine as sulphate, and calculate as lead sulphate. In the filtrate from the lead sulphide determine the alumina and the calcium in the usual manner; caculate the calcium found to calcium sulphate.

Black Pigments.

Black pigments are practically all carbon black in one form or other. They should be tested for oil by washing with ether. Good quality black should be free from oil. Blacks which are alike chemically may behave very differently when ground in thin varnish. For example, lamp-black mixed with such varnish in a ratio of 20 : 100 has flow, while gas-black similarly treated has no flow.

1. *Manufactured Blacks.*—(a) *Moisture.*—Dry 2 grms. for two hours at 105° C. The loss in weight represents the moisture. (b) *Volatile Matter.*—Heat 1 grm. in a well-covered platinum crucible for seven minutes with a Bunsen flame 20 cm. high. The crucible should weigh about 25 grms., have a well-fitting top, and be supported on a platinum triangle 7 cm. above the top of the burner. (c) *Ash.*—Ash 2 grms. preferably in a muffle, and weigh. (d) *Soluble and Insoluble Ash.*—Add to the ash from 2 grms. of black 25 cc. of hydrochloric acid (1 : 1), evaporate to dryness on a steam-bath, add 5 cc. of hydrochloric acid, dilute with 75 cc. of water, filter through a Gooch, wash, ignite, and weigh the insoluble ash. (e) *Adulterations.*—Blacks are occasionally adulterated with Prussian blue. To determine this point boil the sample with 4 per cent sodium hydroxide, filter, render the filtrate acid with hydrochloric acid, and add a solution of a mixture of ferrous and ferric chloride or sulphate. A blue precipitate indicates the presence of Prussian blue. At least one black on the market contains a large amount of a magnetic oxide of iron, which may be readily detected by the action of a magnet. The ash of ivory and bone blacks should contain a large amount of calcium phosphate.

2. *Graphite.*—Graphite is more of a grey pigment than a black. The finer grades are used as lubricants and in making lead pencils. All commercial graphite contains a considerable quantity of ash. For analysis, determine the moisture as usual, boil with hydrochloric acid, filter, dry, and weigh, then ignite; it may be necessary to use oxygen to ensure complete combustion; the loss is taken as carbon. If a previous test has shown the absence of carbonates, the treatment with hydrochloric acid may be omitted. Graphite used as a lubricant is sometimes adulterated with

soft coal. Good Ceylon graphite is practically unaffected by hot sulphuric acid and potassium sulphate, while soft coal is completely decomposed. A fairly good quantitative determination of soft coal in graphite is made as follows:—

Determine the moisture and the ash in one portion, and calculate the total carbon by difference. Treat 1 grm. in a Kjeldahl digestion flask with 30 cc. of strong sulphuric acid and 2 grms. of potassium sulphate. Heat for two hours at a temperature about the fuming point of the sulphuric acid, cool, add water, filter, wash, dry at 105° C., and weigh; then ignite until all of the carbon is burned; the loss here represents the carbon as graphite, and the difference between this determination and that of total carbon represents the soft coal.

(To be continued).

CORRESPONDENCE.

THE CORRELATION OF ROCK AND RIVER-WATER ANALYSES.

To the Editor of the Chemical News.

SIR,—with reference to Mr. Shelton's paper in the CHEMICAL NEWS (vol. cii., p. 75), he has omitted to take at least one important factor into consideration, viz., the sulphates in the drainage water from arable land. Roughly more than a half of ordinary superphosphate consists of sulphate of lime, and 75 per cent of sulphate of ammonia consists of SO_3, and kainit abounds in sulphates; the soil no doubt retains a great amount of these sulphates, and by aid of sun and air elaborates them into the vegetable tissue of sulphur-loving plants, but it cedes enormous quantities to the drainage water. If these factors have not escaped Mr. Shelton's notice, and if he regards them as negligible, he is asking us to believe that not only the sulphuric acid made into sulphate of ammonia in the gas-works, but also the sulphuric acid made into superphosphate, as well as the immense sulphate deposits of Stassfurt, can be simultaneously spread broadcast over the surface of the earth without appreciably affecting the drainage waters, and that to me is to ask too much. The greater part of the organic sulphur of plants passes to the rivers in the urine, &c., and the remainder is washed out of the farmyard dung after application to the soil. But take the leaves and tops of turnips which live and die on the soil which gave the turnip birth, these contribute sulphates to the drainage water. I would recommend Mr. Shelton to read the papers of Lawes and Gilbert, and those of the elder Dr. Voelcker, on drainage water. As to the analyses of the water of rivers which do not receive drainage waters from artificially manured land, it must not be forgotten that wild sulphur-loving plants have a selective power of sulphur absorption. They extract it from the soil, and eventually contribute it as sulphate to the drainage water. They carry sulphates from the soil to the river.

I note also that Mr. Shelton takes no account of the spontaneous oxidation of sulphides (*e.g.*, iron pyrites) into sulphates, nor of sulphur springs in localities showing no sulphur minerals nor rocks like those of Strathpeffer. Again, deep springs in the bed of a river may tap sulphate springs; a river bed is not an impermeable conduit. Neither are lakes free from springs which may or may not contain sulphur.

Mr. Shelton has done good service by calling attention to this important point, and I shall be glad if I have given him the key to the solution of the problem. There are other factors than air and rain and the impurities which they bring down at work, which cannot be ignored, and the solution of the problem is not to be found in the path which Mr. Shelton has mapped out for himself.

A sample of Thames water from the neighbourhood of the Crossness outfall, where they annually use thousands of tons of sulphate of iron, would give quite an erroneous idea of the sulphates in easturine water. As to the River Garforth, alum and green vitriol are there used in recovering fat from wool scourers' soap-suds.

I regret I have to write this hurriedly, and that I have not had time to read Mr. Shelton's paper so thoroughly as I would have desired. I may, however, add that Lawes objected to sulphate of ammonia that it carried lime out of the soil (? as sulphate). I am also well aware that sulphur is built up into hoof, horn, hair, &c., in the animal economy.—I am, &c.,

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9, Parsonage Street, Cubitt Town, London, E.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cl., No. 25, June 20, 1910.

Temperatures of Crystallisation of Binary Mixtures.—E. Baud and L. Gay.—From theoretical considerations the authors have deduced that the lowering of the freezing-point of a binary mixture is proportional to the logarithm of the molecular concentration of the solvent and to the absolute temperature of crystallisation. This conclusion has been verified for the following pairs of liquids:—$C_2H_4Cl_2$ and C_6H_6; $C_2H_4Br_2$ and C_6H_6; $C_6H_5CH_3$ and $C_2H_4Br_2$; ether and $C_2H_4Br_2$.

Photochemical Syntheses of Hydrates of Carbon from Carbon Dioxide and Water in Absence of Chlorophyll.—Daniel Berthellot and Henry Gaudechon.—By the action of the light emitted by a mercury lamp, which is very rich in chemical rays, the authors have induced the assimilation of carbon in absence of chlorophyll. They have thus effected the photosynthesis not only of acids and aldehydes (ternary compounds), but also of the amides (quaternary compounds). This last reaction is of great importance from the point of view of the origin of the albuminous substances in plants which are apparently formed by analogous syntheses.

Relations between Molecular Constitution and Odour.—G. Austenweil and G. Cochin.—From the comparison of the odours of derivatives of citronellol, the authors have found that the odour of roses accompanies the alcoholic function, whether the latter is primary, secondary, or tertiary. Apparently the saturated chains of the fatty series having one or two branches placed identically with regard to the branches of citronellol do not produce the odour of roses—a double bond being absolutely essential. The introduction of a cyclic nucleus seems to have no influence.

Crystallised Aloïnose.—E. Léger.—The author has now found that aloïnose is not a new sugar, but that it is identical with *d*-arabinose, all of the properties of which it possesses. From the reactions of barbaloïn and isobarbaloïn it appears that they are position isomers.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Vinegar.—Can any reader give the formula for making vinegar by present-day methods?—P.

Free Places at the Imperial College of Science and Technology, 1910.—Owing to the summer recess it has been decided to accept entries for the free places until Saturday, October 1st, 1910. Application forms (T.2/268) can be obtained from the Education Officer, London County Council, Victoria Embankment, London, W.C.

THE CHEMICAL NEWS.

Vol. CII., No. 2648.

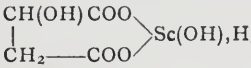
ON SCANDIUM.*

Part II.

By Sir WILLIAM CROOKES, D.Sc., LL.D., For.Sec.R.S.

(Concluded from p. 87).

Scandium Malate,



Malic acid and scandium hydroxide rubbed together with a little water react, and the liquid when heated becomes clear. When gradually cooled a precipitate appears, and at the ordinary temperature of the laboratory the solution is opaque and almost solid. The precipitate consists of very fine granules, having no crystalline appearance under the microscope; it re-dissolves on being heated.

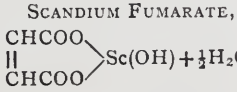
Scandium malate formed in this manner is a granular white powder, soluble in hot and difficultly soluble in cold water. It is easily soluble in ammonia, and is not precipitated from the ammoniacal solution by dilute acetic or malic acid; neither is it precipitated by ammonium sulphide. The aqueous solution dries to a transparent gummy mass when evaporated to dryness. It has a strong mousy odour. The ammoniacal solution also dries to a clear glassy mass, entirely soluble in water.

Analysis.

1. 10·131 gr. of scandium malate dried in a vacuum desiccator lost 0·852 gr. of water after being kept at 110° for twelve hours.
   The same 10·131 gr. of scandium malate, after ignition, left 3·324 gr. of scandia, = 2·152 gr. of scandium.
2. 8·338 gr. of scandium malate, dried in a vacuum desiccator, left on ignition 2·667 gr. of scandia, = 1·727 gr. of scandium.

	Theory.		Experiment.	
			1.	2.
Sc	44·100	20·89	21·24	20·71
$C_4H_5O_6$..	149·040	70·58	70·35 }	79·29
H_2O ..	18·016	8·53	8·41 }	
	211·156	100·00	100·00	100·00

Scandium Fumarate,



Fumaric acid is neutralised with dilute ammonia, and to the warm solution is added an equivalent quantity of scandium sulphate. A white precipitate comes down, which partially re-dissolves on cooling. Scandium fumarate, therefore, like so many other scandium salts, is more soluble in cold than in hot water. The liquid is well boiled, kept for some time in a hot-water oven till the precipitate settles, then quickly filtered and washed with boiling water. After drying in a desiccator at the ordinary temperature, it is powdered, and again exposed to dry air. Scandium fumarate is a white powder, appearing under the microscope as very minute spheres, slightly soluble in hot, more so in cold water, and easily soluble in ammonia. When heated to redness in the air it decomposes quietly, leaving, after the carbon has burnt off, pure white scandia.

The salt is difficult to get to a constant weight; it had to be heated to 105° in a hot-air bath for many days, and the weight taken at intervals of five or six hours. At the end of a fortnight it was still slightly losing weight. I am therefore inclined to think that the half molecule of water may be due to water of crystallisation not entirely driven off at 105°.

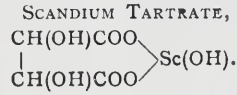
Analysis.

1. 6·254 gr. of scandium fumarate, heated to redness in the air, left 2·287 gr. of scandia, = 1·4810 gr. of scandium.
2. 8·245 gr. of scandium fumarate left on ignition 3·055 gr. of scandia, = 1·9783 gr. of scandium.

	Theory.		Experiment.	
			1.	2.
Sc	44·10	23·95	23·68	23·99
$C_4H_3O_5$.	131·02	76·05	76·32	76·01
$\frac{1}{2}H_2O$ ..	9·01			
	184·13	100·00	100·00	100·00

The scandia obtained in these analyses was tested in the spectrograph, and a minute trace of yttrium and ytterbium lines was just detectable. The earth from the mother-liquor showed the yttrium lines faintly and ytterbium lines strongly. Further experiments are in progress with fumaric acid as a separating agent. Metzger found this acid very effectual in separating thoria from other monazite earths; the present experiments give hopes that it may be useful in separating scandium from ytterbium.

Scandium Tartrate,



Scandium hydroxide is added to a strong solution of tartaric acid with slight warming until the greater part of the scandium hydroxide is dissolved; care must be taken to keep the base in slight excess. The turbid solution is filtered and boiled, when a granular precipitate comes down. This precipitate is well washed with boiling water and dried in a desiccator over sulphuric acid.

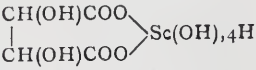
In this way scandium tartrate forms a white crystalline powder, insoluble in hot, slightly soluble in cold water, and insoluble in alcohol. Dried in a desiccator it is anhydrous. When heated it emits the empyreumatic odour peculiar to decomposing tartrates, and leaves a white residue of scandia.

Analysis.

1. 12·149 gr. of scandium tartrate left on ignition 4·027 gr. of scandia, = 2·6078 gr. of scandium.
2. 3·900 gr. of scandium tartrate left on ignition 1·267 gr. of scandia, = 0·8205 gr. of scandium.

	Theory.		Experiment.	
			1.	2.
Sc	44·10	21·09	21·47	21·04
$C_4H_5O_7$ ..	165·04	78·91	78·53	78·96
	209·14	100·00	100·00	100·00

Scandium Racemate,



Scandium racemate is prepared in a similar manner to the tartrate. The two salts, however, are not quite similar. The racemate comes down plentifully on boiling, and it is not anhydrous as is the tartrate, but contains four molecules of water, one of which is driven off at 115°.

Equal weights of tartaric and racemic acids were dissolved in separate bottles of water, and equal quantities of scandium hydroxide added to each bottle, the amount

* A Paper read before the Royal Society, January 20 and June 2, 1910.

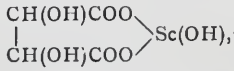
being chosen so that all dissolved except a small quantity, The two bottles were shaken in the cold for half-an-hour, and filtered. The clear solutions were well boiled. A precipitate was formed in each, but that in the tartrate was double that in the racemate.

Analysis.

4·835 gr. of scandium racemate, heated to a temperature of 115° in a hot-air bath, lost 0·322 gr. of water and left on ignition 1·168 gr. of scandia, = 0·7564 gr. of scandium.

	Theory.		Experiment.
Sc	44·100	15·68	15·64
$C_4H_5O_7$ ..	165·040	58·69	77·70
$3H_2O$ . ..	54·048	19·22	
H_2O	18·016	6·41	6·66
	281·204	100·00	100·00

Scandium Lævo-tartrate,



$$CH(OH)COO \atop CH(OH)COO \rangle Sc(OH),2H_2O.$$

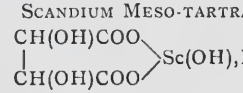
Scandium lævo-tartrate is prepared in a similar way to the tartrate. Dried in a desiccator over sulphuric acid it contains one molecule of water. Dried in the air it contains two molecules of water.

Analysis.

1. 6·252 gr. of scandium lævo-tartrate, dried in a desiccator for twenty-four hours, left on ignition 1·785 gr. of scandia, = 1·1564 gr. of scandium.
2. 7·912 gr. of scandium lævo-tartrate, dried in a desiccator, left on ignition 2·250 gr. of scandia, = 1·4570 gr. of scandium.

	Theory.		Experiment.	
			1.	2.
Sc	44·100	17·99	18·50	18·42
$C_4H_5O_7$.	165·040	67·31	81·50	81·58
$2H_2O$ ..	36·032	14·70		
	245·172	100·00	100·00	100·00

Scandium Meso-tartrate,



$$CH(OH)COO \atop CH(OH)COO \rangle Sc(OH),H_2O.$$

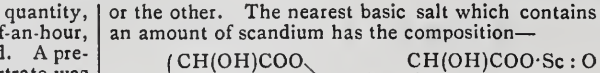
Scandium meso-tartrate is prepared by gently warming a slight excess of scandium hydroxide with aqueous meso-tartaric acid, and then boiling the filtered solution. The meso-tartrate comes down as a white granular precipitate. It is well washed with boiling water and dried over sulphuric acid in a desiccator for twenty-four hours. In this state it contains one molecule of water.

Analysis.

4·899 gr. of scandium meso-tartrate yielded on ignition 1·460 gr. of scandia, = 0·9455 gr. of scandium.

	Theory.		Experiment.
Sc	44·100	19·41	19·30
$C_4H_5O_7$ ..	165·040	80·59	80·70
H_2O . ..	18·016		
	227·156	100·00	100·00

The analysis of the compounds of scandium with tartaric acid and its isomers has been complicated by the tendency to form basic salts admitting of no simple formulæ. Thus, both the tartrate and lævo-tartrate occasionally form salts containing percentages of scandium ranging near to 23·5, with a deviation of two- or three-tenths of a unit one side or the other. The nearest basic salt which contains such an amount of scandium has the composition—



$$5\left\{\begin{matrix} CH(OH)COO \\ | \\ CH(OH)COO \end{matrix}\right\}ScOH + \begin{matrix} CH(OH)COO\cdot Sc:O \\ | \\ CH(OH)COO\cdot Sc:O \end{matrix}$$

and contains 23·49 per cent of scandium.

Scandium αβ-Dibromopropionate,

$(CH_2BrCHBrCOO)_3Sc + (CH_2BrCHBrCOO)_2ScOH.$

I have not prepared either the normal or the basic dibromopropionate in a pure state, but I have obtained a salt corresponding to equimolecular proportions of the two salts, having the above composition. The acid was dissolved in water and exactly neutralised with dilute ammonia. To the warm solution was added dilute scandium nitrate until no more precipitate came down on the addition of either reagent to the filtered solution. Scandium dibromopropionate is almost insoluble in hot or cold water, and, when dried over sulphuric acid in a desiccator, is a white amorphous powder, so easily electrified that it requires great care in powdering and moving it from one vessel to another, or it flies out of the mortar or watch-glasses.

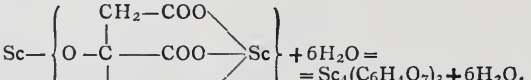
Analysis.

8·117 gr. of scandium dibromopropionate, dried at 110°, yielded on ignition 0·845 gr. of scandia = 0·5598 gr. of scandium.

	Theory.		Experiment.
Sc_2	88·20	7·00	6·90
$C_{15}H_{16}O_{11}Br_{10}$ ..	1171·33	93·00	93·10
	1259·53	100·00	100·00

The filtrate and washings from the precipitated salt were concentrated and precipitated with ammonia. The precipitate was dissolved in nitric acid and examined in the spectrograph, whilst a corresponding test was applied to the scandia from the pure analysed salt. On comparing the two spectrograms, nothing but scandium lines could be detected on that of the scandia from the dibromopropionate, while on that of the earth from the filtrate, yttrium could be detected in minute quantity and ytterbium in larger quantities.

Scandium Citrate,



$$Sc-\left\{O-\begin{matrix} CH_2-COO \\ | \\ C \\ | \\ CH_2-COO \end{matrix}-COO-Sc\right\}_3 + 6H_2O = Sc_4(C_6H_4O_7)_3 + 6H_2O.$$

Ammonium citrate is added to a solution of scandium nitrate in such proportion that no further precipitation takes place on adding either solution. The result is a dense white precipitate, soluble in excess of ammonium citrate solution.

On boiling the filtrate from the scandium citrate a white precipitate comes down, dissolving again when the liquid cools.

The citrate precipitated in the cold was well washed with hot water, filtered, and dried.

When the citrate is dried in the air it contains six molecules of water, and has the composition given above.

When this salt is dried for some days over sulphuric acid it loses two molecules of water and becomes a 4-hydrate salt.

The 4-hydrate salt, heated in an air-bath for six hours to 100°, loses two more molecules of water, and becomes a 2-hydrate.

Analysis.

1. 3·541 gr. of scandium citrate, dried in the air, yielded on ignition 1·140 gr. of scandia, = 0·7382 gr. of scandium.
2. 4·670 gr. of scandium, citrate dried over sulphuric acid for four days, yielded on ignition 1·579 gr. of scandia, = 1·0225 gr. of scandium.

3. 2·797 gr. of scandium citrate, dried over sulphuric acid for four days, yielded on ignition 0·939 gr. of scandia, = 0·6081 gr. of scandium.
4. 3·541 gr. of scandium citrate, heated to 110° for twenty-four hours, lost 0·311 gr. of water.
5. 4·467 gr. of scandium citrate, dried at 100°, yielded on ignition 1·579 gr. of scandia., = 1·0225 gr. of scandium.
6. 3·379 gr. of scandium citrate, dried at 110° for two days, lost 0·149 gr. of water.

Analysis of the 6-Hydrate Citrate.

	Theory.			Experiment. 1.
4Sc	176·40	20·79		20·85
$3(C_6H_4O_7)$	564·10	66·47	79·21	
$6H_2O$ ..	108·10	12·74		79·15
	848·60	100·00		100·00

Analysis of the 4-Hydrate Citrate.

	Theory.		Experiment. 2.	3.	4.
4Sc	176·40	21·71	21·90	21·74	91·22
$3(C_6H_4O_7)$	564·10	69·42	78·10	78·26	
$4H_2O$ ..	72·06	8·87			8·78
	812·56	100·00	100·00	100·00	100·00

Analysis of the 2-Hydrate Citrate.

	Theory.		Experiment. 5.	6.
4Sc	176·40	22·72	22·89	95·59
$3(C_6H_4O_7)$	564·10	72·64	77·11	
$2H_2O$ ..	36·03	4·64		4·41
	776·53	100·00	100·00	100·00

The earth resulting from these analyses was dissolved in nitric acid and tested in the spectrograph; no lines of yttrium or ytterbium could be detected. The mother-liquors were evaporated dry with nitric acid and ignited, and the residual earth tested in the spectrograph; traces were seen of yttrium and much more of ytterbium.

Scandium Orthochlorobenzoate,

$$C_6H_4ClCOOScO+(C_6H_4ClCOO)_2Sc(OH).$$

Orthochlorobenzoic acid is exactly neutralised with ammonia and heated. To the hot solution scandium nitrate is added until no more precipitate comes down on adding a drop either of the ammonia or of the scandium salt. The whole is boiled and allowed to cool. The scandium orthochlorobenzoate forms a white amorphous precipitate, slightly soluble in hot water. It leaves white scandia on ignition in the air.

Analysis.

5·303 gr. of scandium orthochlorobenzoate dried at 105° left on ignition 1·244 gr. of scandia, = 0·8056 gr. of scandium.

	Theory.		Experiment.
Sc_2	88·20	15·01	15·19
$C_{21}H_{13}Cl_3O_8$..	499·48	84·99	84·81
	587·68	100·00	100·00

The scandia used in the preparation of this salt was derived from the quantitative analyses of other organic salts of scandium. Spectrum photographs showed that both the scandia from the precipitated orthochlorobenzoate and that from the mother-liquors were quite free from yttria and ytterbia.

Scandium Metanitrobenzoate,

$$[C_6H_4(NO_2)COO]_3Sc+4H_2O.$$

Metanitrobenzoic acid is neutralised with ammonia, a hot solution of scandium nitrate added till no more precipitate is formed, and the whole boiled for a few minutes. A white crystalline precipitate falls down. The metanitrobenzoate is very slightly soluble in water, and from a hot solution it separates in the form of flat crystals displaying brilliant colours when examined by polarised light. The salt is well washed, drained on blotting-paper, and dried over sulphuric acid in a desiccator.

Analysis.

1. 5·624 gr. of scandium metanitrobenzoate left on ignition 0·607 gr. of scandia, = 0·3931 gr. of scandium.
2. 5·027 gr. of scandium metanitrobenzoate left on ignition 0·543 gr. of scandia, = 0·3516 gr. of scandium.
3. 7·639 gr. of scandium metanitrobenzoate, dried at 110°, lost 0·864 gr. of water, and left on ignition 0·800 gr. of scandia, = 0·5181 gr. of scandium.

	Theory.			Experiments. 1.	2.	3.
Sc	44·10	7·18		6·99	7·00	7·03
$C_{21}H_{12}O_6(NO_2)$	498·13	81·09	92·82	93·01	93·00	81·25
$4H_2O$	72·06	11·73				11·72
	614·29	100·00		100·00	100·00	100·00

The scandia used in these experiments was intentionally not quite pure, being vitiated with a little yttria and ytterbia. On testing, the scandia resulting from the decomposition of the metanitrobenzoate showed no trace of the dominant lines of yttrium or ytterbium, while the earth precipitated from the mother-liquors of the scandium metanitrobenzoate on spectroscopic examination showed strong lines of both impurities. It will be remembered that Neish found that metanitrobenzoic acid was capable of separating thoria from its accompanying earths with quantitative accuracy. Further experiments with this acid are in progress.

Scandium Phthalate,

$$C_6H_4{<}\begin{matrix}COO\\COO\end{matrix}{>}Sc(OH)+H_2O.$$

When a solution of scandium nitrate is added to a solution of ammonium phthalate, an amorphous white precipitate of scandium phthalate comes down. It is slightly soluble in excess of scandium nitrate, and insoluble in water or in excess of ammonium phthalate. Washed and dried in the air it contains one molecule of water and has the composition given above; and after being heated for thirty-six hours to 110° it loses half a molecule of water. Probably a little increase of temperature would have rendered the salt anhydrous. I did not pursue the analysis further.

Analysis.

5·251 gr. of air-dried scandium phthalate lost on drying for thirty-six hours at 110°, 0·192 gr. of water and left on ignition 1·487 gr. of scandia, = 0·9629 gr. of scandium.

	Theory.		Experiment.
Sc	44·10	18·14	18·34
$C_8H_5O_5$ ..	181·04	78·16	78·00
$\frac{1}{2}H_2O$ ..	9·01		
$\frac{1}{2}H_2O$ ..	9·01	3·70	3·66
	243·16	100·00	100·00

The scandia resulting from the above analyses was dissolved in nitric acid and a photograph taken of its spark

spectrum. It was seen to be absolutely pure, with no trace of lines belonging to other earths. The scandia remaining in the filtrate after precipitating the phthalate was examined in the same way, and in its photographed spectrum the dominant lines of yttrium and ytterbium could easily be detected, accompanying the strong scandium spectrum. Experiments are now in progress to find if a satisfactory method of separating scandium from yttrium and ytterbium can be based on this reaction.

Scandium Tetrachlorophthalate,

$$C_6Cl_4{<}^{COO}_{COO}{>}Sc(OH) + 6H_2O.$$

On mixing together equivalent proportions of scandium nitrate and ammonium tetrachlorophthalate a dense white amorphous precipitate comes down, almost insoluble in hot or cold water. When washed and dried in the air scandium tetrachlorophthalate has the composition given above.

Analysis.

4·830 gr. of scandium tetrachlorophthalate left on ignition 0·692 gr. of scandia, = 0·4481 gr. of scandium.

	Theory.		Experiment.
Sc	44·10	9·36	9·28
$C_8HCl_4O_5$.	318·85	90·64	90·72
$6H_2O$ ..	108·10		
	471·05	100·00	100·00

The scandia left on ignition was tested in the spectrograph and found to be quite pure. Yttrium and ytterbium could be detected in the earth obtained from the filtrate left after precipitating the tetrachlorophthalate.

Scandium 2-Nitrophenyl-4′-tolylamine-4-sulphonate,

$$\left\{CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3{<}^{NO_2}_{SO_3}\right\}_2 Sc(OH) + 5H_2O.$$

The sodium salt of this acid is dissolved in water and a solution of scandium nitrate added. If the solutions are strong, a red precipitate falls; if weak, the mixture must be concentrated. On cooling, the scandium salt separates in feathery crystals of a fine scarlet colour. It must be purified by re-crystallisation from a hot aqueous solution. The crystals are slightly soluble in cold water.

Heated in an air-bath at 105° for forty-eight hours, the scarlet crystals assume an orange-yellow colour, losing water and becoming anhydrous.

On being further heated, the salt decomposes rather suddenly, with intumescence, leaving a carbonaceous residue, which at a red heat gradually burns white, leaving scandia.

Analysis.

1. 1·154 gr. of the scandium salt lost on heating 0·136 gr. of water. When heated to redness the same salt left 0·108 gr. of scandia, = 0·0699 gr. of scandium.
2. 0·863 gr. of the salt, heated to 105°, lost 0·095 gr. of water.

	Theory.			Experiment.	
				1.	2.
Sc ..	44·10		5·76	6·06	
26C ..	312·00				88·99
23H ..	23·18				
11O ..	176·00	631·36	82·47	82·15	
4N ..	56·04				
2S ..	64·14				
$5H_2O$.	90·08		11·77	11·79	11·01
	765·54		100·00	100·00	100·00

Scandium Octamethyl Tetramino Dihydroxy Paradixanthyl Benzene Tetracarboxylate,

$$\left.\begin{array}{l} C_{40}H_{38}O_4N_4{<}^{COO}_{COO}{>}ScOH \\ \qquad\qquad\quad COO{-}Sc{:}O \\ C_{40}H_{38}O_4N_4{<}^{COO}_{COO}{>}ScOH \\ \qquad\qquad\quad COO{-}Sc{:}O \\ \qquad\qquad\quad COO{>}ScOH \end{array}\right\} = C_{88}H_{79}O_{29}N_8Sc_5.$$

Naturally this is a question of considerable scientific interest. How would scandium behave when combined as a salt with a highly complex acid? In Dr. Silberrad's recently published paper on "The Condensation Products of Mellitic Acid with Meta-amino Phenol," (*Journ. Am. Chem. Soc.*, February, 1910, No. 2, p. 189) some highly complex bodies are described; it became interesting to determine precisely what basicity scandia would assume towards polycarboxylic acids of this nature.

By the kindness of Dr. Silberrad I have had an opportunity of experimenting with octamethyl tetramino-dihydroxy paradixanthyl benzene tetracarboxylic acid.

Previous experiments would lead one to expect the scandium salt of this acid to have the composition $C_{44}H_{40}O_{14}N_4Sc_2$. This I could not prepare, the salt produced by metathesis containing more scandium than this formula admits of. The only scandium salt I could form of this acid has the composition shown above.

Octamethyl tetramino dihydroxy paradixanthyl benzene-tetracarboxylic acid is a dark red powder, insoluble in water and easily soluble in dilute ammonia. The solution in ammonia, very slightly alkaline, is exactly neutralised with acetic acid; to the hot solution scandium acetate is added and the whole boiled. On cooling, scandium octamethyl tetramino dihydroxyparadixanthyl benzene tetracarboxylate comes down as a red powder, insoluble in cold water.

Analysis.

3·167 gr. of scandium octamethyl tetramino dihydroxy-paradixanthyl benzene tetracarboxylate left on ignition 0·576 gr. of scandia, = 3·3730 gr. of scandium.

	Theory.		Experiment.
Sc_5	220·50	11·41	11·78
$C_{88}H_{79}O_{29}N_8$ ..	1711·71	88·59	88·22
	1932·21	100·00	100·00

More than once I have been asked why I chose such very out-of-the-way acids wherewith to prepare scandium salts? I give my chief reason:—Attempts on several occasions have been made to discover a means of separating some of the "rare earths" from their companions by forming compounds with weak organic acids. Thus, in 1897, Kosmann (*Chem. Centralb.*, 1897, Part I., 837; Chemical News, lxxxvi., 218) employed citric acid in the separation of thoria. Urbain (*Bull. Soc. Chim.*, 1896, xv., 347) used acetylacetonate of sodium for the same purpose. Metzger (*Journ. Am. Chem. Soc.*, xxiv., No. 10; Chemical News, lxxxvi., 218, 229, 242) tried maleic acid, cinnamic acid, picric acid, phthalic acid, and fumaric acid. He found fumaric acid effectual in separating thoria from the other earths in monazite, whilst the other acids also gave partial separations, although not complete.

In 1904, Neish (*Journ. Am. Chem. Soc.*, xxvi., No. 7; Chemical News, xc., 196, 201) tried many organic acids for the separation of the rare earths, chiefly thoria. Among other acids, he tried gallic, tannic, citric, salicylic, oleic, linoleic, paratoluic, oxyisophthalic, benzoic, meta-, ortho-, and para-nitrobenzoic, and fumaric. Of these the metanitrobenzoic acid proved most effectual, the process being capable of accurate quantitative results. It was found that other rare earths besides thoria behave differently towards these acids, but the variation was not sufficient to enable the reactions to be used for accurate separations.

Soon after those experimental papers appeared I commenced similar researches hoping to find an organic reagent which would be a precipitant for some of the yttria earths—if not with quantitative accuracy, at all events with sufficient separation to allow a fractionation method to be based on the reaction. My results, not being sufficiently definite, were never published; but as the organic acids were in my laboratory when the scandium research was commenced, I preferred to use these acids, of which the purity and the history were known, rather than start afresh with acids of unknown history.

Many of the acids were prepared and purified by myself; for others I am under obligations to friends, among whom I must specially thank Dr. O. Silberrad.

I wish also to express warm thanks to Dr. von Martius for the munificent gift of 103 gr. of almost pure scandia—a gift which has enabled me to work on a larger scale, and to preserve many specimens of analysed salts for future reference.

THE DETERMINATION OF ANTIMONY.

By E. G. BECKETT, Ph.D., Dipl.Chem.

This article is a short abstract of the author's doctorial thesis, and the details of the analytical work are omitted, but they are described at length in the original ("Inaugural Dissertation," by E. G. Beckett, Zürich, 1909, Gebr. Leeman and Co., Zürich).

The object of the research was to ascertain the degree of accuracy obtainable in the various methods in use for the exact determination of antimony, and it was necessary to select a compound of that metal which could be prepared in absolute purity and of constant composition, and which could be analysed with great accuracy without reference to atomic weights, because the results obtained in the early stages of the work seemed to raise a doubt as to the reliability of the currently accepted atomic weight of antimony. A compound fulfilling these conditions was found in antimony trisulphide, and a large part of the work was devoted to the preparation of the pure substance and to an accurate determination of its composition. A comparison of the various methods proposed for the exact estimation of antimony was then proceeded with.

An extended search in the literature of the subject revealed the fact that another observer, Youtz (*Zeit. Anorg. Chem.*, 1903, p. 337), had found reason to believe that the value found by Dumas and by Kessler, and formerly in use, was the more correct one. The author's reasons for sharing this view will appear in the course of this article.

The description of the work is arranged for convenience of reference in the following divisions :—

A. 1. Preparation of Pure Antimony Trisulphide.
   2. Analysis of Pure Antimony Trisulphide.

B. Determination of Antimony.
   1. As Trisulphide, Sb_2S_3.
   2. Volumetrically with Iodine Solution.
   3. As Tetroxide, Sb_2O_4.
   4. As Pentoxide, Sb_2O_5.

A. 1. *Preparation of Pure Antimony Trisulphide.*

The material used for the preparation of the trisulphide was pure commercial tartar emetic which was found to contain 0·12 per cent of lead. On re-crystallising the tartar emetic it was found that the whole of the lead was precipitated with the crystals, the mother-liquor being practically free from this impurity. Fractional crystallisation would have afforded a means of obtaining tartar emetic free from lead, but a quicker and more effective method was found in stirring small quantities of freshly prepared sulphuretted hydrogen water into a boiling concentrated solution of tartar emetic at intervals of an hour, until a filtered sample of the liquid gave a clear solution with an excess of sodium sulphide. The whole solution was then filtered hot, and the crystals which separated out on cooling were re-crystallised three times, and were then found to contain no foreign metal.

Crystallised tartar emetic has no permanently definite composition; after having been freed from mother-liquor by pressing between filter-paper and allowed to dry in air in a thin layer for two days, the crystals contained a little less than one molecule of water per molecule of $C_4H_4O_7SbK$, and somewhat less than half a molecule after similar exposure for a fortnight. The salt became anhydrous on lying over phosphorus pentoxide in a desiccator for three months.

The antimony sulphide precipitated by sulphuretted hydrogen from solutions of tartar emetic containing hydrochloric acid was always found to contain chlorine. Various methods of precipitation from various concentrations of solution were tried, but in all cases the antimony sulphide contained chlorine which could not be removed by washing. Prolonged boiling of the precipitate with sulphuretted hydrogen water containing acetic acid removed some of the chlorine, but very slowly. F. Henz (*Zeit. Anorg. Chem.*, 1903, p. 1) had already found that it is necessary to precipitate the sulphide from boiling solutions containing mineral acid, otherwise a finely divided product results, which is difficult to wash.

It was found that heating the washed and dried precipitated antimony trisulphide to 300° C. in a stream of CO_2 reduced the amount of chlorine.

	Per cent chlorine in antimony trisulphide.	
	Dried at 100–110° C.	After heating to 300° C.
1. Precipitated according to Henz	0·6—1·2	0·18—0·3
2. Precipitated according to Vortman and Metzl (*Zeit. Anal. Chem.*, 1905, xliv., 525)—		
(*a*) Solution boiled until the precipitate became brown	1·27	0·50
(*b*) Solution boiled until the precipitate became black	0·90	0·18—0·35
(*c*) Solution boiled for three hours after the precipitate had become black	0·64	0·37

Vortman and Metzl precipitate the antimony sulphide from a boiling solution containing 20 per cent concentrated hydrochloric acid; the precipitate which is first of a yellowish colour becomes red, then brown, and at last black.

The determination of the chlorine was carried out as follows :—

The antimony trisulphide was dissolved in caustic potash and potassium tartrate, and oxidised with an excess of 30 per cent hydrogen peroxide (perhydrol of Merck), the solution was then acidified with nitric acid, and boiled to destroy the excess of H_2O_2, after which the chlorine was precipitated with silver nitrate.

After many trials I succeeded in obtaining the pure substance by melting the precipitated antimony trisulphide in a stream of sulphuretted hydrogen free from hydrogen; by this treatment the amount of chlorine was reduced to 0·03 per cent.

As this purified product was to be used as a standard by which the determinations of antimony were to be compared, it was above all neccssary to determine accurately how much antimony and sulphur this pure antimony trisulphide contained.

A. 2. *Analysis of Antimony Trisulphide.*

The antimony was determined by heating the Sb_2S_3 in a stream of hydrogen, a method used by Schneider (*Pogg. Ann.*, xcviii., 293) in his determination of the atomic weight of antimony. The sulphide is hereby reduced to metallic antimony, and the amount thus found is independent of atomic weights. The reduction was carried out in

a bulb of hard glass, which was heated in an iron air-bath. The reaction begins at about 350° C., and the temperature was slowly raised to about 600° C. 0·07 to 0·1 per cent of sulphur remained in the antimony, and could not be removed by prolonged heating.

The determination of the sulphur in the trisulphide presented many difficulties, and it was only after much work that a satisfactory method was found. I proceeded as follows:—

The antimony sulphide was slowly burned in a current of air, and the resultant gas containing the sulphur as dioxide was filtered through quartz sand in order to remove the finely divided antimony oxide which was carried along with it. The SO_2 was absorbed in ammonia, and oxidised to sulphuric acid with bromine or hydrogen peroxide. The oxide of antimony was tested for sulphur by dissolving it in a mixture of hydrochloric and hydriodic acids (in which it dissolves with ease), and evaporating until all the iodine and most of the acid were driven off. The residue was dissolved in tartaric acid, and barium chloride added. No sulphur could thus be detected in the oxide.

The absorption of the sulphur dioxide by ammonia was very troublesome to begin with, as dense clouds of ammonium sulphite formed which were difficult to retain. They were found to be easily absorbed by passing the gases through a layer of glass-wool impregnated with dilute ammonia. The sulphuric acid was precipitated as barium sulphate, and both the barium sulphate in the filtrate and the barium chloride in the precipitate were determined.

Summary of Results.

	Antimony trisulphide precipitated according to Henz.	Antimony trisulphide precipitated according to Vortman and Metzl.	Pure antimony trisulphide.
Sb ..	71·71	71·68	71·65
S ..	27·95	28·07	28·33
Cl ..	0·24	0·18	0·03
C ..	—	—	0·01
	99·90	99·93	100·02

B. 1. *Determination of Antimony as Trisulphide*, Sb_2S_3.

There are chiefly two methods of carrying out this determination:—

1. Precipitation as red amorphous antimony trisulphide as recommended by Henz.

2. Precipitation as black crystalline antimony trisulphide as recommended by Vortman and Metzl.

The weight of trisulphide obtained by both of these methods agrees very well with the amount of pure antimony trisulphide used for the determinations. The above analyses also show that both precipitates contain the same amount of antimony, namely, 71·7 per cent.

Following figures show the amount of chlorine present in antimony trisulphide when precipitated in small quantities (0·25 grm.).

	Per cent Cl in antimony sulphide	
	Dried at 100–120° C.	Heated to 300° C. in CO_2.
Precipitated according to Henz..	1·11	0·30
Precipitated according to Vortman and Metzl	0·38	0·22

Although the dried red Sb_2S_3 contains more chlorine than the black, the results are the same, as most of the chlorine is driven off by heating to 300° C. without appreciable loss of antimony.

After many determinations have been carried out according to Henz's method in the same glass heating tube, a minute sublimate of antimony sulphide collects in the narrow part of the tube. This sublimate must be caused by the chlorine in the precipitate, as pure antimony sulphide melts at 440° C. without subliming.

Petriciolli and Reuter found that the loss on heating antimony trisulphide to 300° C. in a stream of CO_2 was so great that they condemned the method. This loss on heating may have been due to the presence of chlorine, which varies with the amount of tartaric acid used in the precipitation of the trisulphide. I therefore examined the influence of tartaric acid, and found that the weight of trisulphide obtained by Henz's method is likely to be too low when less than 4 molecules of tartaric acid are present in the precipitation of 1 molecule of antimony, but the results obtained by the Vortman and Metzl method are not influenced at all by tartaric acid. The chlorine is given off as hydrochloric acid gas on heating the antimony trisulphide precipitate in a stream of carbonic acid, and when much hydrochloric acid gas is present a part of this reacts on the trisulphide with the production of volatile antimony trichloride. The reaction is minimised by slow heating in a rapid current of a neutral gas, and it may be that the denser condition of the Vortman and Metzl precipitate enables the hydrochloric acid gas to be carried away more quickly. The method of Vortman and Metzl is much to be preferred to that of Henz, for the results are more concordant and the determination is quicker and more convenient, the precipitate obtained being dense and easy to wash, ordinary distilled water being also admissible for that purpose.

In determining antimony by these methods truer results are obtained when the atomic weight of antimony is taken as being 122 (Dumas and Kessler) instead of 120·2, which is at present in use.

	Per cent Sb in Sb_2S_3.
Found (see above)	71·7
Calculated (Sb = 120·2) ..	71·43
Calculated (Sb = 122) ..	71·73

A. Fischer (*Zeit. Anorg. Chem.*, 1904, p. 363) condemns the trisulphide method. He determined the sulphur in a precipitated red antimony trisulphide and assumed the difference to be antimony. He found:—

S	= 28·00
Sb (by difference)	= 72·00

The amount of sulphur is correct, but according to my own analysis of a similar preparation, the difference is really made up of antimony and chlorine. I found:—

Sb	= 71·71
S	= 27·95
Cl	= 0·24
	99·90

B. 2. *The Volumetric Determination of Antimony with Iodine by Mohr's Method.*
("Mohr-Classen," 7 Aufl., p. 340).

The determination depends upon the fact that iodine in presence of sodium bicarbonate oxidises a solution of antimony trioxide in tartaric acid to antimony pentoxide:—
$Sb_2O_3 + 4I + 4NaHCO_3 = Sb_2O_5 + 4NaI + 2H_2O + 4CO_2$.

The solution of iodine in potassium iodide was standardised with a solution of sodium thiosulphate, which was standardised with pure iodine (after Treadwell, *Lehrb.*, ii., 496).

Forty cc. of a saturated solution of sodium bicarbonate were always added to the neutral solution to be titrated. The method of titration was modified in all possible ways, but whether the iodine was added to the tartar emetic or the tartar emetic to the iodine, or if an excess of iodine was added and titrated back with thiosulphate immediately or after standing, *the results were always the same.*

The results, which were very concordant, were always 1 per cent too low when calculated with the figure 120·2 as the atomic weight of antimony.

The first results were obtained by titrating solutions of tartar emetic, and as the solutions were not fresh it was thought that a part of the antimony might have become oxidised to antimony pentoxide; it was found, however, that a freshly prepared solution gave exactly the same results again after standing for three months. That is not the case with a hydrochloric acid solution of antimony tri-

chloride, for that was found to have become oxidised to pentachloride to the extent of 2·73 per cent in four months. There was still a possibility that the dry tartar emetic used might contain some antimony pentoxide, and this point was investigated by precipitating the antimony with H_2S, and heating the washed and dried Sb_2S_3 to 300° C. in an atmosphere of carbonic acid in order to convert any pentasulphide present into trisulphide. The trisulphide was then dissolved in hydrochloric acid in a flask with a reflux condenser and boiled until all H_2S was expelled. The solution containing therefore all the antimony as trichloride was then neutralised, treated with tartaric acid and excess of sodium bicarbonate, and titrated with iodine. As exactly same amount of antimony was found after this treatment as before, the tartar emetic must have been free from pentoxide of antimony.

The Volumetric Determination of Antimony by Weller's Method (Ann. Chem. Pharm., 1882, p. 363).

Weller determines antimony in the condition of pentachloride by reduction with HI, and titration of the liberated iodine after distillation.

Mohr's method depends on the oxidation of antimony trioxide to pentoxide, and we have in Weller's method a means of performing the reverse reaction, so that a comparison of results by the two methods affords a check on the completeness of the oxidation according to Mohr, since special experiments were made which went to prove that the reduction of antimony pentachloride to trichloride by Weller's method is a complete one.

A solution of antimony pentachloride free from trichloride was prepared according to Bunsen by oxidising an alkaline solution of antimony with chlorine in excess. The solution was then evaporated on a water-bath with addition of concentrated hydrochloric acid three times, in order to decompose completely any chlorate formed. The acid residue was taken up with pure hydrochloric acid, and diluted with water. Carefully measured equal portions of this solution were used for the following determinations :—

1. The amount of antimony present was determined by the trisulphide method already described under B. 1, according to Vortman and Metzl.

2. The solution was distilled with KI and HCl in the apparatus of Gooch (*Zeit. Anorg. Chem.*, 1897, xiii., 101), and the iodine obtained was titrated with thiosulphate.

The amount of iodine thus found bore exactly the same relation to the antimony present as that required to oxidise the antimony trioxide in tartar emetic to pentoxide in Mohr's method. Here again the results obtained by Weller's method also came out 1 per cent too low, when the calculation was based on the figure 120·2 as the atomic weight of antimony, but the discrepancy disappears when the older value 122 is employed.

The atomic weight 122 was also deduced from results obtained by using Mohr's method of determining antimony. Carefully weighed quantities of the pure preparation of antimony trisulphide (containing 71·65 per cent Sb) were dissolved in pure hydrochloric acid, nearly neutralised, treated with tartaric acid and excess of sodium bicarbonate, and titrated with iodine solution. The following figures were obtained :—

Sb_2S_3 taken. Grm.	Iodine required. Grm.	Atomic weight of antimony deduced.
0·4056	0·60527	122·08
0·3311	0·49419	122·04
0·3670	0·54834	121·87
0·3654	0·54517	122·12
0·2717	0·40494	122·28
	Mean =	122·08

The calculation is based on 126·97 as the atomic weight of iodine and 32·06 as the atomic weight of sulphur.

The time which would be required for a re-determination of the atomic weight of antimony was not at my disposal, and I submit the results obtained in the course of this investigation as being sufficient to raise a doubt as to the accuracy of the value accepted at the present time. In this view I am supported by the conclusions arrived at by Youtz (*Zeit. Anorg. Chem.*, 1903, p. 337), who also found a deficiency in results obtained volumetrically when based on the value 120·2. In fact, I was so convinced of the correctness of the higher figure for the atomic weight of antimony that I adopted it for the rest of the work which follows:

B. 3. *Determination of Antimony as Tetroxide.*

The material used was the pure preparation of antimony trisulphide containing 71·65 per cent Sb. It was oxidised with nitric acid, and the greater part of the acid was driven off by evaporation. Excess of ammonia solution was stirred into the pasty mass, and the whole was then evaporated, dried in an air-bath, and ignited. The product was free from sulphur. After ignition for an hour over a blowpipe the weight of the oxide became quite constant, but was about 0·6 per cent higher than that required for Sb_2O_4. After heating in an Hereaus electrical furnace to 700—760° C. the results were lower, but still too high. The mean of six experiments gave Sb_2O_4, equivalent to 72·02 per cent Sb instead of the true amount 71·65 per cent. I found on distilling the Sb_2O_4 with HCl and KI, and titrating the liberated iodine, that more oxygen was present than that corresponding to Sb_2O_3+O. Theoretically, the tetroxide should contain 5·19 per cent of active oxygen, whereas I found 5·49 per cent; that is, an excess of 0·30 per cent of oxygen above that corresponding to Sb_2O_4. The product also contained 0·28 per cent of hygroscopic moisture. When a correction was made for the moisture and the excess of oxygen, the Sb_2O_4 was equivalent to 71·62 per cent Sb in the Sb_2S_3 taken, which is sufficiently near the true amount, 71·65 per cent. In other experiments the composition of the Sb_2O_4 obtained from antimony trisulphide containing chlorine was found to be subject to practically the same correction.

The temperature obtained by heating over the blowpipe is not sufficiently uniform for the quantitative production of such a compound as Sb_2O_4, which, according to Baubigny (*Comptes Rendus*, 1897, cxxiv., 499), is only formed at 750—800° C. and decomposes at 950° C. Henz's experiments show that the weight of small quantities of tetroxide never becomes constant over the blowpipe. In my experiments I found that in quantities of about 1 grm. the weight of tetroxide became constant under these conditions, but was always too high by containing oxygen in excess of that corresponding to Sb_2O_4.

B. 4. *Determination of Antimony Pentoxide.*

Vortman and Metzl (*Zeit. Anal. Chem.*, 1905, p. 525) proposed igniting the precipitated antimony sulphide with a mixture of ferric oxide and ferric nitrate, in order to obtain antimony pentoxide mixed with ferric oxide for weighing, but I could not get satisfactory results with this method. The mixture of ferric oxide and ferric nitrate was moist and yet hygroscopic, and could therefore not be weighed accurately. I also found it impossible to prepare a sufficiently homogeneous mixture to begin with, for on igniting it alone in order to determine the amount of ferric oxide in it, I got very varying results. My attempts to modify did not lead to success. A mixture of the antimony trisulphide with ferric oxide was treated with nitric acid, and ignited; the trisulphide was ignited with basic ferric nitrate; in both cases the results came out about 3 per cent too high. The nearest approach to accuracy was reached by igniting the Sb_2S_3 with a mixture of ferric oxide and mercuric oxide, but the results were always too high, and the weight of the residual mixture never became really constant.

Summary of Conclusions.

1. The most accurate method of determining antimony is by precipitation as trisulphide, and weighing it as such. The method of Vortman and Metzl is preferable to that of Henz from its greater convenience and degree of accuracy.

2. Antimony trisulphide precipitated from hydrochloric acid solutions always contains chlorine, which cannot be removed by washing. The amount of this chlorine is greatly reduced by heating the precipitate to 300° C. in a stream of CO_2, after which the Sb_2S_3 generally contains from 0·15 to 0·3 per cent Cl.

3. The volumetric determination of antimony with iodine gives very concordant results, but these are only correct when the older atomic weight of antimony (Sb = 122) is used. When the atomic weight is taken as being 120·2 the results are about 1 per cent too low.

4. The determination of antimony as tetroxide is unreliable when a blowpipe is used for the ignition. The method may give good results if the oxide is heated in a furnace giving a uniform temperature of between 800° and 900° C., but means have to be adopted to prevent the absorption of hygroscopic moisture during the process of weighing.

5. The determination of antimony as pentoxide is not reliable.

SOME VARIATIONS IN THE OFFICIAL METHOD FOR THE DETERMINATION OF VOLATILE MATTER IN COAL.*

By A. C. FIELDNER and J. D. DAVIS.

(Concluded from p. 93).

Influence of Composition of Gas.

In order to determine the influence of composition of fuel-gas, determinations were made over 20 cm. coal-gas flame and 20 cm. natural gas flame, each gas being supplied to the burner at its proper pressure.

The natural gas analysed as follows :—

Carbon dioxide	0·1
Paraffin hydrocarbons..	98·6
Nitrogen	1·3
	100·00

The coal-gas taken from the mains of the gas company that supplies artificial gas in Pittsburg, Pa., analysed—

Unsaturated hydrocarbons.. ..	7·5
Carbon dioxide	1·5
Oxygen	0·2
Carbon monoxide..	8·9
Methane	44·8
Hydrogen	33·7
Nitrogen	3·4
	100·00

Both series of volatile determinations were made by the same analyst, using the same apparatus, the only difference being in the fuel-gas used. The results are shown in Table VI.

The temperatures are practically the same, and the variations in volatile matter average zero. It should be noted, however, that the natural gas was supplied to a carefully regulated burner at 13 inches pressure. If the comparisons were made at the lower pressures usually found in laboratories, the results by natural gas would be decidedly lower.

Table VII. gives a comparison of volatile matter obtained on the same samples of coal, in two different laboratories of the Geological Survey. The Pittsburg laboratory used natural gas at 13 inches water pressure with a Tyrell burner; the Washington laboratory used illuminating gas at 2 inches pressure with the Fletcher burner. The height of flame was 20 cm. in each case.

From the previous experiment on natural and coal-gas closely agreeing results would be expected. Such, however, was not the case. As shown in the table, the Washington series averaged 1·2 per cent higher than the Pittsburg. The maximum temperature of 970° C., noted in the Washington laboratory, was 120° higher than noted with either coal or natural gas at the Pittsburg laboratory. It had been supposed that the Washington illuminating gas was of a similar composition to that of the Pittsburg coal-gas. This assumption, however, proved to be erroneous, as shown by the following analysis :—

TABLE VI.—*Difference due to Using Natural or Coal-gas.*

Coal No.	Per cent volatile. Coal-gas, 2·5 ins. pressure.	Natural gas, 13 ins. pressure.	Difference.
	(*a*) Fletcher Burner.		
1	17·0	17·2	+0·2
2	17·1	17·0	−0·1
6	33·0	32·8	−0·2
4	31·5	31·8	+0·3
5	31·7	31·5	−0·2
		Average	0·0
	(*b*) Tyrell Burner.		
1	16·7	17·0	+0·3
6	32·3	32·6	+0·3
4	31·6	31·3	−0·3
5	31·4	31·5	+0·1
7	4·5	4·3	−0·2
		Average	+0·04
Temp. °C.	855	850	

TABLE VII.—*Comparison of Results obtained in different Laboratories.*

Coal No.	Per cent volatile matter. Pittsburg. Natural gas, 13 ins. pressure. Tyrell burner.	Washington. Illuminating gas. 2·5 ins. pressure. Fletcher burner.	Difference.
1	17·0	18·3	+1·3
2	16·8	18·2	+1·4
3	17·0	18·8	+1·8
4	31·3	32·5	+1·2
5	31·5	32·6	+1·1
6	32·6	33·4	+0·8
7	4·3	5·3	+1·1
10	17·7	18·7	+1·0
		Average	+1·2
Temp. °C.	850	970	

TABLE VIII.—*Analysis of Washington Illuminating Gas.*

	Per cent.
Carbon dioxide	3·0
Unsaturated hydrocarbons.. ..	10·4
Oxygen	1·0
Carbon monoxide..	27·6
Methane	19·0
Hydrogen	33·1
Nitrogen	5·9
	100·0

The Washington gas consists entirely of carburetted water-gas. It contains 26 per cent less methane and 19 per cent more carbon monoxide than coal-gas. The replacement of methane by carbon monoxide decreases the flame volume very materially, and since the height of flame is the same in both cases, the heating effect of a low methane gas is, under ordinary laboratory conditions, considerably greater.

Chikashiga and Matsumato (*Journ. Soc. Chem. Ind.*, 1904, xxiii., January 30, p. 50) call attention to the disadvantages of uncarburetted water-gas as a laboratory fuel on account of the high temperature of the flame produced,

* Presented by permission of the Director, U.S. Geological Survey. From the *Journal of Industrial and Engineering Chemistry*, ii., No. 7.

They state that "comparatively thick copper wire and sheet, and even thin platinum wire, are easily melted and hard glass easily worked in its flame."

Another factor that may have contributed to the difference in temperature noted in the two laboratories is the surface condition of the platinum crucible. Constam, in a paper (*Journ. fur Gasbel.*, 1909, October 9, p. 889) communicated to the Seventh International Congress of Applied Chemistry, mentions "that the slower rise and the lower final temperature in dull platinum crucibles caused the yield of coke in them to be greater than in polished platinum crucibles."

As the crucibles used in all the experiments at the Pittsburg laboratory were very dull and tarnished in appearance, it was decided to polish them and then run some determinations to check Constam's conclusions. The results are given in Table IX.

TABLE IX.—*Comparison of Volatile Matter produced in the same Crucible before and after Polishing.*

Coal No.	Per cent volatile. Before.	After.	Difference.
10	17·0	18·1	1·1
3	17·0	18·1	1·1
6	32·6	33·3	0·7
Temp. °C.	845	890	45

Temperature Measurements (° C.). Coal No. 1.

Time, in minutes.	Before polishing.		After polishing.
0·5	250	320	240
1	530	550	590
1·5	670	690	750
2	780	780	840
2·5	825	825	880
3	840	840	890
3·5	848	848	890
4	850	848	890
4·5	850	848	890
5	850	848	890
6	850	847	890
7	850	845	890

TABLE X.—*Volatile Matter by Distillation.*

Test No.	Time, in minutes.	Vacuum.	Per cent volatile moisture.
1.	30	¾ in. Hg	18·3 (*a*)
2.	45	,,	18·7 (*b*)
3.	45	,,	19·4 (*b*)
4.	45	,,	18·2 (*b*)
5.	40	4 ins. H_2O	18·8 (*b*)
6.	45	Atmospheric pressure	18·7 (*c*)
		Average..	18·7
7.	7	Atmosphere of CO_2	18·5 (*d*)
8.	7	,, ,,	18·3 (*d*)
9.	7	,, ,,	18·6 (*d*)
		Average..	18·5
		Official method ..	19·3

(*a*) Retort weighed.
(*b*) Coke weighed.
(*c*) Gradual heat.
(*d*) 30-grm. platinum crucible heat treatment as in Official Method.

In tests Nos. 1 to 6 inclusive, a sample of Pocahontas coal was subjected to destructive distillation in an iron retort, made from a piece of 1-inch gas-pipe, capped at one end and tubulated at the other. The retort was heated by means of a train of Bunsen burners to a bright red-heat in a furnace of asbestos board. A 20-grm. charge was used.

Tests Nos. 7 to 9 inclusive were made in a 30-grm. platinum crucible with a tubulated cover; carbon dioxide was kept passing through during the determination; the heat treatment was exactly the same as in the official method. Both retort and crucible tests give results somewhat lower than the official method, although not materially.

Summary.

The results of these experiments may be briefly summarised as follows:—

Two laboratories are likely to vary 2 per cent in volatile matter, both using the official method. The percentage of volatile matter obtained from the same sample of coal varies with the temperature and rate of heating. This is not sufficiently defined by height of flame. Temperatures ranging from 760° C. to 890° C. may be attained with a 20 cm. natural gas flame, when the gas pressure is varied from 1 to 13 inches of water; variations of 2 per cent volatile matter are thus produced. Difference in type and size of burner influence results from 0·3 to 1·5 per cent.

Polished crucibles become hotter and yield about 1 per cent more volatile matter than dull grey ones.

Laboratories using natural gas are apt to get results on volatile matter that are considerably lower than those using coal-gas, unless the following precautions are observed:—

1. Gas should be supplied to the burner at a pressure of not less than 10 inches of water.
2. Natural gas burners admitting an ample supply of air should be used.
3. Gas and air should be regulated so that a flame with a short, well-defined inner cone is produced.
4. The crucibles should be supported on platinum triangles and kept in well-polished condition.

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,*

INCLUDING PAINTS AND PAINT MATERIALS, INKS, LUBRICATING OILS, SOAPS, &c.

By PERCY H. WALKER.

(Continued from p. 82).

PAINTS (*continued*).

Coloured Pigments.

1. *Yellow, Orange, and Red Pigments.*—The most important yellow pigment is chrome yellow, which varies in shade from a light lemon yellow to a deep orange. The lighter shades generally contain lead sulphate as well as lead chromate, while the deep orange contains some basic lead chromate. Pure chrome yellow should contain only lead chromate, lead sulphate, and possibly some basic lead in the darker shades. (Lead sulphate may be replaced by other insoluble lead compounds. A chrome yellow should be considered adulterated if it contains anything besides insoluble lead compounds). Zinc yellow is zinc potassium chromate of a composition approximating the following formula: $(ZnCrO_4)_3K_2Cr_2O_7$.

(a) *Chrome Yellow.*—(1) *Moisture.*—Dry 2 grms. for two hours at 105° C. (2) *Insoluble Impurities.*—Treat 1 grm. with 20 cc. of strong hydrochloric acid, cover and heat on a steam-bath for fifteen minutes, add 100 cc. of hot water, boil (the solution should be complete), filter, wash, ignite, and weigh the insoluble impurities. (3) *Lead.*—Evaporate the filtrate from the insoluble to about 2 cc., but not to dryness, add 100 cc. of 95 per cent alcohol, stir, allow to stand for one hour, cool in ice-water, filter on a Gooch crucible, wash with 95 per cent alcohol, dry for one hour at 110° C., cool, and weigh as lead chloride. Add 0·0085 grm. to the weight of the lead chloride to correct for its solubility in alcohol. Multiply the result thus obtained by 0·74478 to obtain the amount of lead present. (4) *Chromium.*

* *Bulletin* No. 109, Revised, U.S. Department of Agriculture, Bureau of Chemistry.

—Evaporate the filtrate from the lead chloride determination to dryness on a steam-bath to expel the alcohol, add about 5 cc. of hydrochloric acid, then about 50 cc. of water, and warm till the solution is complete. Cool, transfer to a volumetric flask, and make up to a definite volume. To an aliquot add sodium peroxide in sufficient amount to render the solution alkaline and to oxidise the chromium to chromate, boil until all of the hydrogen peroxide is driven off, cool, make acid with sulphuric acid, add a measured excess of standard ferrous sulphate, and titrate the excess of iron with standard potassium dichromate. (5) *Sulphate.*—In another aliquot of the filtrate from the lead chloride determination, determine the sulphate in the ordinary way by precipitation and weigh as barium sulphate. (Some chromes contain barium phosphate instead of lead sulphate, in which case test for phosphoric acid. Or barium sulphate, calcium sulphate, &c., may replace lead sulphate. Lead citrate is also sometimes present instead of lead sulphate). (6) *Treatment in the Presence of Soluble Impurities.*—If the sample contains no soluble impurities, the preceding method will give a complete analysis. When the qualitative test shows calcium it may be necessary to make the analysis in a somewhat different manner, for gypsum would by this treatment be precipitated with the lead chloride and render the determination worthless. In such a case dissolve and separate the insoluble as above. Dilute the filtrate from the insoluble to 400 cc., cool, pass in a rapid stream of hydrogen sulphide until all of the lead is precipitated as lead sulphide, filter, wash with water containing some hydrogen sulphide, dissolve the lead sulphide in dilute nitric acid (hot), add an excess of sulphuric acid, heat to fumes, and complete the determination of lead as sulphate in the usual way. In the presence of chromium the solution must be very dilute and the hydrogen sulphide passed in rapidly to get a good separation of lead as sulphide. Transfer the filtrate from the lead sulphide to a 500 cc. flask, add ammonium hydroxide until it is slightly alkaline, pass in hydrogen sulphide until all of the zinc present is precipitated (in case no zinc is present the addition of hydrogen sulphide is unnecessary); make up to volume, mix, allow to settle, draw off aliquots of the clear liquid, and determine the calcium (and, if necessary, the magnesium) in the usual way. All the zinc and chromium will still be in the 500 cc. flask; dissolve in hydrochloric acid, make up to the mark, mix, take out an aliquot, and determine the zinc volumetrically by the ferrocyanide method as described under lead zinc whites. In another aliquot determine chromium as already described. Sulphate can be determined by dissolving another portion in hydrochloric acid, filtering from it the insoluble, and precipitating with barium chloride from the dilute hot filtrate; if the solution is kept dilute and hot, the barium sulphate precipitate will not be contaminated by lead.

(b) *Zinc Yellow.*—(1) *Moisture.*—Dry 2 grms. for two hours at 105° C. (2) *Insoluble Impurities.*—To 1 grm. of the dry pigment add 25 cc. of strong ammonium hydroxide, stir well, and dilute to about 100 cc. with water, stir frequently for about thirty minutes, carefully breaking up all lumps, but do not heat. Filter and wash with dilute ammonium hydroxide and then with water, dry residue at 105° C. to constant weight, and weigh, then ignite and weigh again. If desired, dissolve the residue in hydrochloric acid and analyse in the usual manner. (3) *Soluble Zinc, Chromium, and Potassium.*—Heat the filtrate from the determination of insoluble impurities to boiling in a graduated flask, pass in hydrogen sulphide until all of the chromate is reduced and the zinc is precipitated as zinc sulphide and chromium as chromium hydroxide. Fill to the mark, mix, allow to settle, draw out an aliquot of the clear liquid, and determine alkalis by adding sulphuric acid, evaporating to dryness, igniting, and weighing as mixed sulphates. If desired, potassium may be determined as potassium platinic chloride (K_2PtCl_6). Add hydrochloric acid to the residue in the flask and determine zinc and chromium as in chrome yellow. (4) *Impure Samples.*—The preceding methods will serve only for samples which are pure or adulterated only with substances insoluble in ammonium hydroxide. Very impure samples should be examined as described under chrome yellow (see above).

(c) *Red Lead and Orange Mineral.*—These pigments in the pure state are oxides of lead (approximately Pb_3O_4), being probably mixtures of compounds of varying proportions of lead monoxide and lead dioxide. Moisture, insoluble impurities, and total lead may be determined by the methods given under chrome yellow; or, in the absence of alkaline earth metals, the lead may be determined as sulphate in nitric acid solution (dissolve by adding a few drops of hydrogen dioxide) by evaporating with an excess sulphuric acid until fumes of sulphuric anhydride are evolved. Determine as sulphate in the usual way. The lead dioxide (PbO_2) may be determined as follows:—Weigh 0·5 grm. of the very finely ground pigment into a 150 cc. Erlenmeyer flask. Mix in a small beaker 15 grms. of crystallised sodium acetate, 1·2 grms. of potassium iodide, 5 cc. of water, and 5 cc. of 50 per cent acetic acid. Stir until all is liquid, pour into the Erlenmeyer flask containing the lead, and rub with a glass rod until all of the lead is dissolved; add 15 cc. of water, and titrate with tenth-normal sodium thiosulphate, using starch as indicator. A small amount of lead may escape solution at first, but when the titration is nearly complete this may be dissolved by stirring. The reagents should be mixed in the order given, and the titration should be carried out as soon as the lead is in solution, as otherwise there is danger of loss of iodine. One cubic centimetre of tenth-normal sodium thiosulphate corresponds to 0·011945 grm. of lead dioxide, or 0·034235 grm. of red lead (Pb_3O_4). These coloured lead pigments may have their colour modified by the addition of organic colouring matters. As a general rule, such adulteration may be detected by adding 20 cc. of 95 per cent alcohol to 2 grms. of the pigment, heating to a boil, and allowing to settle. Pour off the alcohol, boil with water, and allow to settle, then use very dilute ammonium hydroxide. If either the alcohol, water, or ammonium hydroxide is coloured, it indicates organic colouring matter. The quantitative determination of such adulteration is difficult and must generally be estimated by difference.

(d) *Vermilion.*—True vermilion, or, as it is generally called, English vermilion, is sulphide of mercury. On account of its cost it is rarely used in paints, and is liable to gross adulteration. It should show no bleeding on boiling with alcohol and water and no free sulphur by extraction with carbon disulphide. A small quantity mixed with five or six times its weight of dry sodium carbonate and heated in a tube should show globules of mercury on the cooler portion of the tube. The best test for purity is the ash, which should be not more than one-half of 1 per cent. Make the determination in a porcelain dish or crucible, using 2 grms. of the sample. Ash in a muffle or in a hood with a very good draft, as the mercury fumes are very poisonous. It is seldom necessary to make a determination of the mercury; but if this is required it may be determined by mixing 0·2 grm. of the vermilion with 0·1 grm. of very fine iron filings, or better "iron by hydrogen." Mix in a porcelain crucible and cover with a layer 10 mm. thick of the iron filings, place the crucible in a hole in an asbestos sheet so that it goes about half way through, cover with a weighed, well-fitting, gold lid which is hollow at the top, fill this cavity with water, heat the crucible for fifteen minutes with a small flame, keep the cover filled with water, cool, remove the cover, dry for three minutes at 100° C., and thirty minutes in a desiccator, and weigh. The increase in weight is due to mercury. The mercury can be driven off from the gold by heating to about 450° C. A silver lid may be used, but gold is much better.

Another method is to place in the closed end of a combustion tube, 45 cm. long and 10 to 15 mm. in diameter, a layer of 25 to 50 mm. of roughly pulverised magnesite, then a mixture of 10 to 15 grms. of the vermilion with four or five times its weight of lime, followed by 5 cm. of

Determination of Red Colours in Organic Lake.

Reagent.	Source of colour.				
	Alizarin.	Eosin.	Para-nitraniline.	Ortho-anisidine.	Scarlet (2R).
Sulphuric acid (conc.)	Dark brown, with reddish undertone, becoming light yellow on diluting.	Changes to yellow; fluorescent solution with excess of sodium hydroxide.	Purple; colour returning on diluting.	Purple; red on diluting.	Darkened; lighter on diluting.
Hydrochloric acid (conc.)	Colour becomes "muddy."	Changes to yellow; reddish fluorescent solution with excess of sodium hydroxide.	Colour slightly darkened; lighter on diluting.	Dark purplish red; lighter on diluting.	Darkened; lighter on diluting.
Sodium hydroxide (conc. sol.)	Dark reddish brown; little change on diluting.	Little change; fluorescent solution on diluting.	Colour changed to brownish red; light red on diluting.	Little change.	Reddish solution on diluting.
Alcohol	Insoluble.	Reddish fluorescent solution.	Slight yellowish orange solution.	—	Slight reddish solution.
Sodium hydroxide (conc.) and alcohol	Purplish; dark brown on diluting.	—	Purple; colour returning on diluting.	Little change.	Colour darker; reddish solution on diluting.

lime, and plug the tube with asbestos. Draw out the end of the tube and bend it over at an angle of about 60°. Tap the tube so as to make a channel along the top, and place it in a combustion furnace with the bent neck down, resting with its end a little below some water in a small flask or beaker. Heat first the lime layer, and carry the heat back to the mixture of lime and pigment. When all the mercury has been driven off, heat the magnesite, and the evolved carbon dioxide will drive out the last of the mercury vapours. Collect the mercury in a globule, wash, dry, and weigh.

Genuine vermilion is at the present time little used in paints. Organic lakes are used for most of the brilliant red, scarlet, and vermilion shades. These organic colouring matters are sometimes precipitated on red lead, orange mineral, or zinc oxide; but as a usual thing the base is barytes, whiting, or china clay. Paranitraniline red, a compound of diazotised paranitraniline and beta-naphthol is largely employed; but a number of colours may be used. To test for red colours in such a lake the method from Hall may be of value ("The Chemistry of Paints and Paint Vehicles," p. 29), though other colours may be employed, which makes the accompanying table of only limited use.

It is well also to try the action of reducing and oxidising agents such as stannous chloride, ferric chloride, &c. (see Zerr, Bestimmung von Teerfarbstoffen in Farblacken; also Schultz and Julius, "A Systematic Survey of the Organic Colouring Matters").

Paranitraniline red is soluble in chloroform. It is also well to try the solvent action on different reds of sodium carbonate, &c. The amount of organic pigment present in such reds is generally very small, and when it cannot be determined by ignition owing to the presence of lead, zinc, or carbonate, it is best determined by difference.

(To be continued).

Power of Adsorption of the Hydroxides of Silicon, Aluminium, and Iron.—Paul Rohland.—The power of adsorption of the hydroxides of silicon, aluminium, and iron, especially of silicon, is a property of talcs as well as of clays, though to a lesser degree. The talcs must be regarded as acid salts of metasilicic acid corresponding to the formula $Mg_2H_2(SiO_3)_4$. It was found that talcs adsorb the colloidal dissolved substances in blood, beer, starch, &c., also all dye-stuffs of complicated composition, coal-tar dyes, vegetable and animal dyes. Neither ions of weak acids, nor crystalloids, nor coloured substances of simple composition were adsorbed.—*Zeit. Anorg. Chem.*, May 18.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift fur Anorganische Chemie.
Vol. lxvii., No. 1, May 18, 1910.

Cryoscopic Determinations at Low Temperatures (−40° to −117°).—E. Beckmann and P. Waentig.—For cryoscopic experiments at temperatures which lie below the freezing-point of mercury (−39°) the pentane thermometer does not appear to be satisfactory. A platinum resistance thermometer is much more reliable, and its sensitiveness increases as the temperature falls. To measure the resistance the compensation method was adopted, a Deprez-D'Arsonval galvanometer being used. Cymol and toluol were found satisfactory for determining the cryoscopic constants. The results of the experiments are given in the following table:—

	Freezing-point in °C.	Cryoscopic const. in 0° C.	Latent heat of vap. in cal.
Carbon tetrachloride	−24	298	4·17
Pyridine	−40	49·7	21·8
Chloroform	−61	46·8	46·8
Ether	−117	17·9	27·4
Hydrogen iodide ..	−51	202·6	4·31
,, bromide .	−86	94·1	7·44
,, chloride .	−112	49·8	10·3
,, sulphide .	−82·9	38·3	18·8

The degree of dissociation of a solvent seems to be independent of the temperature. Hydrocarbon derivatives, like carbon tetrachloride and chloroform, resemble benzene in their low dissociating power. Hydrocarbons give normal constants and molecular weights with all these substances, while alcohol gives smaller constants and correspondingly larger molecular weights. Ether, which on boiling gives the normal molecular weight for substances containing hydroxyl, also gave the normal constants on freezing at −117°. In frozen chloroform the molecule of acetic ether shows no special tendency to associate. The molecular weight of iodine in its brown pyridine solution almost always corresponded to I_2. In this case the production of an addition product could not be directly proved. The halogen hydrides are solvents which possess only a weak

dissociating power; in contrast to dissolved hydrocarbons substances containing hydroxyl, *e.g.*, thymol, alcohol, acetic acid, and benzoic acid, show a tendency towards association. The specific conductivity of the pure solvent increases from the hydrides of iodine, bromine, and chlorine, reaching the value $0{\cdot}2 \times 10^{-6}$ with the last. On dissolving substances which show cryoscopically an enlarging of the molecule the conductivity is many times increased. This appears to confirm the assumption of Steele, McIntosh, and Archibald that the conductivity depends upon the dissociation of complex molecules which result in the solution. Sulphuretted hydrogren is a solvent of very low dissociating power, and in its solution electrical conductivity cannot be proved. Hydrocarbons gave normal constants; substances containing OH moderate association. Benzophenone in dilute solution gave values which might point to a lowering of the number of molecules.

Detection and Determination of very small Amounts of Silver.—G. Stafford Whitby.—All solutions of silver salts when heated with caustic soda and certain organic substances give a yellow or brown coloration even if only one part of silver is present in 25,000,000 parts. The organic substances are dextrin, gum arabic, cellulose, starch, and cane-sugar. Some drops of a fairly concentrated sugar solution are added to 50 cc. of the solution, the beaker is heated for two minutes on a water-bath, six drops of a normal solution of caustic soda are added, and it is again heated for twenty to thirty seconds. The colour of the solution is then compared with that of a solution containing a known amount of silver. Ammonia must not be present, but the other metals investigated did not affect the coloration, which is due to the presence of colloidal silver. Probably the caustic soda converts the silver into the hydroxide, which then reacts directly with the organic substances, a hydrogen ion of the organic molecule is split off and forms water with the hydroxyl ion of the silver hydroxide, while the silver, robbed of its ionic charge, goes into colloidal solution.

Thermo-electricity of Alloys.—E. Rudolfi. — The author has determined the thermo-electric force of the following alloys in order to determine the relationship between the thermo-electric properties and the constitution of alloys:—(1) Tin-cadmium, (2) zinc-tin, (3) zinc-cadmium, (4) tin-lead, (5) bismuth-cadmium, (6) lead-antimony, (7) gold-silver, (8) gold-copper, (9) copper-nickel, (10) platinum-palladium. The results of this investigation are given in a series of tables and diagrams, showing the thermo-electric forces at 150° and 100° towards both nickel and copper as a function of the concentration. The results show that—(1) If the two components of a binary alloy do not mix in the crystalline condition, the relation of thermo-electric force to concentration is expressed by a straight line. (2) If the two components form an uninterrupted series of mixed crystals, and thus the solidified alloys consist of homogeneous crystals of the composition of the original mixture, the thermo-electric force curve is U-shaped. (3) If the alloy consists of mixed crystals only at certain concentrations the curve consists of two straight lines, the first sloping towards and the other away from the concentration axis. Similarly, if the two components form a compound the two straight lines forming the curve meet at the concentration corresponding to the compound; the curve is concave to the concentration axis.

MISCELLANEOUS.

Professorship of Chemistry in the University of Queensland.—Queensland was separated from New South Wales in December, 1859, and celebrated last December the completion of her first half century of independent existence within the Empire, and the Queenslanders have decided to commemorate this event by the foundation of a University to form the forefront of this educational and scientific advance. The Government (a Labour one) is giving large subsidies and handing over the old Government House and grounds for a first home. The authorities naturally are anxious to begin well, and to vigorous young chemists with a little pioneering spirit about them, who will take a deep interest in the teaching of their young men and in the many special problems of the young country, the opportunity here presented is one of a life-time. The following are conditions of the appointment and general particulars in connection with this Professorship:—1. The title of the gentleman appointed will be "Professor of Chemistry." 2. The Professor will be required to give such instruction and to conduct such examinations as the Senate may from time to time direct, and to exercise such supervision over the work of his Department as the Senate may from time to time determine. 3. The Professor will be required to devote the whole of his time to the work of his Department, but he may, by permission of the Senate, undertake such private work as does not, in the opinion of the Senate, interfere with the proper discharge of his University duties. Under ordinary circumstances, permission to undertake private work will be limited to the long vacation. 4. The salary of the Professor will be £900 per annum, payable monthly, subject to a deduction not exceeding 10 per cent for the purchase of an endowment assurance in favour of the Professor. 5. A residence or quarters will not be provided by the Senate. 6. The Professor shall not be entitled to any participation in lecture fees. 7. The tenure of office of the Professor shall depend upon his good behaviour, subject to the following limitations:—(*a*) If the Professor shall become, in the opinion of the Senate, incapacitated for performing the duties of his office, the Senate shall be at liberty to appoint a substitute temporarily and to determine the terms of such appointment; the substitute shall be paid from the Professor's emoluments. Should the Professor become, in the opinion of the Senate, unfit for further duty, the Senate may terminate his services. (*b*) The Senate shall have an absolute right to terminate the Professor's services at any time after he has attained the age of sixty years, should they consider that course necessary. (*c*) The Senate shall have absolute power to remove the Professor from office for misconduct, of which the Chancellor shall be the sole judge. (*d*) Should the Professor desire to resign his office, he shall give the Senate at least six months' notice of his intention. 8. The Professor shall not take any part in political affairs otherwise than by the exercise of the franchise. 9. Each candidate must state when he would be prepared to enter upon his duties. It is desirable that the Professor should, if possible, be on duty by January 1st, 1911, or as soon as possible thereafter, so as to organise the work of his Department before the first term of the University begins—namely, the second Tuesday in March, 1911. 10. The salary will begin from January 1st, 1911; if the Professor is unable to commence duty on that date, the salary will begin from the date on which the Professor reports himself personally to the Registrar as ready to commence duty. 11. If the Professor appointed shall come from Europe or America, the sum of £100 will be allowed in full for travelling expenses. 12. Applications in duplicate from candidates resident tn Australasia must reach the Registrar, University of Queensland, Brisbane, not later than August 31st, 1910. Applications in duplicate from Europe or America must reach the Agent-General for Queensland, Queensland Government Offices, Marble Hall, 409 and 410, Strand, London, W.C., not later than August 31st, 1910. The applications must be endorsed "Application for Professorship, University of Quesnsland." 13. Each applicant must state his age, supply full particulars as to his education, degrees, teaching experience, and general qualifications; furnish certified copies of his certificates and testimonials, and forward a medical certificate certifying to his physical fitness.—J. D. STORY, Chairman Administrative Committee, University of Queensland, Brisbane, May 19, 1910.

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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

SHEFFIELD, 1910.

INAUGURAL ADDRESS OF THE PRESIDENT,

The Rev. Prof. T. G. Bonney, Sc.D., LL.D., F.R.S.

Thirty-one years have passed since the British Association met in Sheffield, and the interval has been marked by exceptional progress. A town has become a city, the head of its municipality a Lord Mayor; its area has been enlarged by more than one-fifth; its population has increased from about 280,000 to 479,000. Communication has been facilitated by the construction of nearly thirty-eight miles of electric tramways for home service and of new railways, including alternative routes to Manchester and London. The supplies of electricity, gas, and water have more than kept pace with the wants of the city. The first was just being attempted in 1879; the second has now twenty-three times as many consumers as in those days; the story of the third has been told by one who knows it well ("History and Description of Sheffield Water Works," W. Terrey, 1908), so that it is enough for me to say your water supply cannot be surpassed for quantity and quality by any in the kingdom. Nor has Sheffield fallen behind other cities in its public buildings. In 1897 your handsome Town Hall was opened by the late Queen Victoria; the new Post Office, appropriately built and adorned with material from almost local sources, was inaugurated less than two months ago. The Mappin Art Gallery commemorates the munificence of those whose name it bears, and fosters that love of the beautiful which Ruskin sought to awaken by his generous gifts. Last, but not least, Sheffield has shown that it could not rest satisfied till its citizens could ascend from their own doors to the highest rung of the educational ladder. Firth College, named after its generous founder, was born in the year of our last visit; in 1897 it received a charter as the University College of Sheffield, and in the spring of 1905 was created a University, shortly after which its fine new buildings were opened by the late King; and last year its library, the generous gift of Dr. Edgar Allen, was inaugurated by his successor, when Prince of Wales. I must not now dwell on the great work which awaits this and other new universities. It is for them to prove that, so far from abstract thought being antagonistic to practical work, or scientific research to the labour of the factory or foundry, the one and the other can harmoniously co-operate in the advance of knowledge and the progress of civilisation.

You often permit your President on these occasions to speak of a subject in which he takes a special interest, and I prefer thus trespassing on your kindness to attempting a general review of recent progress in science. I do not, however, propose, as you might naturally expect, to discuss some branch of petrology; though for this no place could be more appropriate than Sheffield, since it was the birthplace and the lifelong home of Henry Clifton Sorby, who may truly be called the father of that science. This title he won when, a little more than sixty years ago, he began to study the structure and mineral composition of rocks by examining thin sections of them under the microscope.* A rare combination of a singularly versatile and active intellect with accurate thought and sound judgment, shrewd in nature, as became a Yorkshireman, yet gentle, kindly, and unselfish, he was one whom his friends loved and of whom this city may well be proud. Sorby's name will be kept alive among you by the Professorship of Geology which he has endowed in your University; but, as the funds will not be available for some time, and as that science is so intimately connected with metallurgy, coal-mining, and engineering, I venture to express a hope that some of your wealthier citizens will provide for the temporary deficiency, and thus worthily commemorate one so distinguished.

But to return. I have not selected petrology as my subject, partly because I think that the great attention which its more minute details have of late received has tended to limit rather than to broaden our views, while for a survey of our present position it is enough to refer to the suggestive and comprehensive volume published last year by Mr. A. Harker ("The Natural History of Igneous Rocks," 1909); partly, also, because the discussion of any branch of petrology would involve so many technicalities that I fear it would be found tedious by a large majority of my audience. So I have preferred to discuss some questions relating to the effects of ice which had engaged my attention a dozen years before I attempted the study of rock slices. As much of my petrological work has been connected with mountain districts, it has been possible for me to carry on the latter without neglecting the former, and my study of ice-work gradually led me from the highlands into the lowlands.* I purpose, then, to ask your attention this evening to some aspects of the glacial history of Western Europe.

At no very distant geological epoch the climate in the northern part of the earth was much colder than it is at present. So it was also in the southern; but whether the two were contemporaneous is less certain. Still more doubtful are the extent and the work of the ice which was a consequence, and the origin of certain deposits on some northern lowlands, including those of our own islands, namely, whether they are the direct leavings of glaciers or were laid down beneath the sea by floating shore-ice and bergs. Much light will be thrown on this complex problem by endeavouring to ascertain what snow and ice have done in some region which, during the Glacial Epoch, was never submerged, and none better can be found for this purpose than the European Alps.

At the present day one school of geologists, which of late years has rapidly increased in number, claims for glaciers a very large share in the sculpture of that chain, asserting that they have not only scooped out the marginal lakes, as Sir A. Ramsay maintained full half a century ago, but have also quarried lofty cliffs, excavated great cirques, and deepened parts of the larger Alpine valleys by something like two thousand feet. The other school, while admitting that a glacier, under special circumstances, may hollow out a tarn or small lake and modify the features of rock scenery, declares that its action is abrasive rather than erosive, and that the sculpture of ridges, crags, and valleys was mainly accomplished in pre-glacial times by running water and the ordinary atmospheric agencies.

In all controversies, as time goes on, hypotheses are apt to masquerade as facts, so that I shall endeavour this evening to disentangle the two, and call attention to those which may be safely used in drawing a conclusion.

In certain mountain regions, especially those where strong limestones, granites, and other massive rocks are dominant, the valleys are often trench-like, with precipitous sides, having cirques or corries at their heads, and with rather wide and gently sloping floors, which occasionally descend in steps, the distance between these increasing with that from the watershed. Glaciers have unquestionably occupied many of these valleys, but of late years they have been supposed to have taken a large share in excavating them. In order to appreciate their action we must imagine the glens to be filled up and the district

* His subsequent investigations into the microscopic structure of steel and other alloys of iron, in the manufacture of which your city holds a foremost place, have been extended by Mr. J. E. Stead and others, and they, besides being of great value to industrial progress, have thrown important sidelights on more than one dark place in petrology.

* May I add that hereafter a statement of facts without mention of an authority means that I am speaking from personal knowledge.

restored to its former condition of a more or less undulating upland. As the mean temperature* declined snow would begin to accumulate in inequalities on the upper slopes. This, by melting and freezing, would soften and corrode the underlying material, which would then be removed by rain and wind, gravitation and avalanche. In course of time the hollow thus formed would assume more and more the outlines of a corrie or a cirque by eating into the hill-side. With an increasing diameter it would be occupied, as the temperature fell, first by a permanent snowfield, then by the *névé* of a glacier. Another process now becomes important, that called "sapping." While ordinary glacier-scour tends, as we are told, to produce "sweeping curves and eventually a graded slope," "sapping" produces "benches and cliffs, its action being horizontal and backwards," and often dominant over scour. The author of this hypothesis (W. D. Johnson, *Science*, N.S., 1899, ix., pp. 106, 112) convinced himself of its truth in the Sierra Nevada by descending a *bergschrund* 150 feet in depth, which opened out, as is so common, beneath the walls of a cirque. Beginning in the *névé*, it ultimately reached the cliff, so that for the last thirty feet the bold investigator found rock on the one hand and ice on the other. The former was traversed by fracture planes, and was in all stages of displacement and dislodgment; some blocks having fallen to the bottom, others bridging the narrow chasm, and others frozen into the *névé*. Clear ice had formed in the fissures of the cliff; it hung down in great stalactites; it had accumulated in stalagmitic masses on the floor. Beneath the *névé* the temperature would be uniform, so its action would be protective, except where it set up another kind of erosion, presently to be noticed; but in the chasm, we are informed, there would be, at any rate for a considerable part of the year, a daily alternation of freezing and thawing. Thus the cliff would be rapidly undermined and be carried back into the mountain slope, so that before long the glacier would nestle in a shelter of its own making. Farther down the valley the moving ice would become more effective than sub-glacial streams in deepening its bed; but since the *névé*-flow is almost imperceptible near the head, another agency must be invoked, that of "plucking." The ice grips, like a forceps, any loose or projecting fragment in its rocky bed, wrenches that from its place, and carries it away. The extraction of one tooth weakens the hold of its neighbours, and thus the glen is deepened by "plucking," while it is carried back by "sapping." Streams from melting snows on the slopes above the amphitheatre might have been expected to co-operate vigorously in making it, but of them little account seems to be taken, and we are even told that in some cases the winds probably prevented snow from resting on the rounded surface between two cirque-heads.† As these receded, only a narrow neck would be left between them, which would be ultimately cut down into a gap or "col." Thus a region of deep valleys with precipitous sides and heads, of sharp ridges, and of more or less isolated peaks is substituted for a rather monotonous, if lofty, highland.

The hypothesis is ingenious, but some students of Alpine scenery think more proof desirable before they can accept it as an axiom. For instance, continuous observations are necessary to justify the assumption of diurnal variations of temperature sufficient to produce any sensible effect on rock at the bottom of a narrow chasm nearly fifty yards deep and almost enclosed by ice. Here the conditions would more probably resemble those in a *glacière*, or natural ice cave. In one of these, during the summer, curtains and festoons of ice depend from the walls; from them and from the roof water drips slowly, to be frozen into stalagmitic mounds on the floor, which is itself sometimes a thick bed of ice. On this the quantity of fallen rock *débris* is not greater than is usual in a cave, nor are the walls notably shattered, even though a gap some four yards deep may separate them from the ice. The floors of cirques, from which the *névé* has vanished, cannot as a rule be examined, because they are masked by *débris* which is brought down by the numerous cascades, little and big, which seam their walls; but glimpses of them may sometimes be obtained in the smaller corries (which would be cirques if they could), and these show no signs of either "sapping" or "plucking," but some little of abrasion by moving ice. Cirques and corries also not infrequently occur on the sides as well as at the heads of valleys; such, for instance, as the two in the *massif* of the Uri Rothstock on the way to the Surenen Pass and the Fer à Cheval above Sixt. The Lago di Ritom lies between the mouth of a hanging valley and a well-defined step, and just above that is the Lago di Cadagno in a large steep-walled corrie, which opens laterally into the Val Piora, as that of the Lago di Tremorgio does into the southern side of the Val Bedretto. Cirques may also be found where glaciers have had a comparatively brief existence, as the Creux des Vents on the Jura; or have never been formed, as on the slopes of Salina, one of the Lipari Islands, or in the limestone desert of Lower Egypt (A. J. Jukes-Browne, *Geol. Mag*, 1877, p. 477). I have seen a miniature stepped valley carved by a rainstorm on a slope of Hampstead Heath; a cirque, about a yard in height and breadth, similarly excavated in the vertical wall of a gravel pit; and a corrie, measured by feet instead of furlongs, at the foot of one of the Binns near Burntisland, or, on a much reduced scale, in a bank of earth. On all these the same agent, plunging water, has left its marks—runlets of rain for the smaller, streams for the larger; convergent at first, perhaps, by accident, afterwards inevitably combined as the hollow widened and deepened. Each of the great cirques is still a "land of streams," and they are kept permanent for the greater part of the year by beds of snow on the ledges above its walls.

The "sapping and plucking" process presents another difficulty—the steps already mentioned in the floors of valleys. These are supposed to indicate stages at which the excavating glacier transferred its operations to a higher level. But, if so, the outermost one must be the oldest, or the glacier must have been first formed in the lowest part of the incipient valley. Yet, with a falling temperature, the reverse would happen, for otherwise the snow must act as a protective mantle to the mature pre-glacial surface almost down to its base. However much age might have smoothed away youthful angularities, it would be strange if no receptacles had been left higher up to initiate the process; and even if sapping had only modified the form of an older valley, it could not have cut the steps unless it had begun its work on the lowest one. Thus, in the case of the Creux de Champ, if we hesitate to assume that the sapping process began at the mouth of the valley of the Grande Eau above Aigle, we must suppose it to have started somewhere near Ormont Dessus, and to have excavated that gigantic hollow, the floor of which lies full 6000 feet below the culminating crags of the Diablerets.

But even if "sapping and plucking" were assigned a comparatively unimportant position in the cutting out of cirques and corries, it might still be maintained that the glaciers of the Ice Age had greatly deepened the valleys of mountain regions. That view is adopted by Professors Penck and Brückner in their work on the glaciation of the Alps ("Die Alpen in Eiszeitalter," 1909), the value of which even those who cannot accept some of their conclusions will thankfully admit. On one point all parties agree—that a valley cut by a fairly rapid stream in a durable rock is V-like in section. With an increase of speed the walls become more vertical; with a diminution the valley widens and has a flatter bed, over which the river, as the base-line is approached, may at last meander. Lateral streams will plough into the slopes, and may be numerous enough to convert them into alternating ridges and furrows. If a valley has been excavated in thick horizontal beds of rock varying in hardness, such as limestones and shales, its sides exhibit a succession of terrace walls and shelving banks, while a marked dip and other

* In the remainder of this Address "temperature" is to be understood as mean temperature. The Fahrenheit scale is used.

† This does not appear to have occurred in the Alps.

dominant structures produce their own modifications. It is also agreed that a valley excavated or greatly enlarged by a glacier should be U-like in section. But an Alpine valley, especially as we approach its head, very commonly takes the following form:—For some hundreds of feet up from the torrent it is a distinct V; above this the slopes become less rapid, changing, say, from 45° to not more than 30°, and that rather suddenly. Still higher comes a region of stone-strewn upland valleys and rugged crags, terminating in ridges and peaks of splintered rock, projecting from a mantle of ice and snow. The V-like part is often from 800 to 1000 feet in depth, and the above-named authors maintain that this, with perhaps as much of the more open trough above, was excavated during the Glacial Epoch. Thus the floor of any one of these valleys prior to the Ice Age must often have been at least 1800 feet above its present level.* At a rough estimate we may fix the deepening of one of the larger Pennine valleys, tributary to the Rhone, to have been during the Ice Age, at least 1600 feet in their lower parts. Most of them are now hanging valleys; the stream issuing, on the level of the main river, from a deep gorge. Their tributaries are rather variable in form; the larger, as a rule, being more or less V-shaped; the shorter, and especially the smaller, corresponding more with the upper part of the larger valleys; but their lips generally are less deeply notched. Whatever may have been the cause, this rapid change in slope must indicate a corresponding change of action in the erosive agent. Here and there the apex of the V may be slightly flattened, but any approach to a real U is extremely are. The retention of the more open form in many small elevated recesses, from which at the present day but little water descends, suggests that where one of them soon became buried under snow,† but was insignificant as a feeder of a glacier, erosion has been for ages almost at a standstill.

The V-like lower portion in the section of one of the principal valleys, which is all that some other observers have claimed for the work of a glacier, cannot be ascribed to subsequent modification by water, because ice-worn rock can be seen in many places, not only high up its sides, but also down to within a yard or two of the present torrent.

Thus valley after valley in the Alps seems to leave no escape from the following dilemma:—Either a valley cut by a glacier does not differ in form from one made by running water, or one which has been excavated by the latter, if subsequently occupied, is but superficially modified by ice. This, as we can repeatedly see in the higher Alpine valleys, has not succeeded in obliterating the physical features due to the ordinary processes of erosion. Even where its effects are most striking, as in the Spitallamm below the Grimsel Hospice, it has not wholly effaced those features; and wherever a glacier in a recent retreat has exposed a rock surface, that demonstrates its inefficiency as a plough. The evidence of such cases has been pronounced inadmissible, on the ground that the glaciers of the Alps have now degenerated into senile impotence; but in valley beds over which they passed when in the full tide of their strength the flanks show remnants of rocky ridges only partly smoothed away, and rough rock exists on the "lee-sides" of ice-worn mounds which no imaginary plucking can explain. The ice seems to have flowed over rather than to have plunged into the obstacles in its path, and even the huge steps of limestone exposed by the last retreat of the Unter Grindelwald Glacier have suffered little more than a rounding off of their angles, though that glacier must have passed over them when in fullest development, for it seems impossible to explain these by any process of sapping.

* The amount varies in different valleys; for instance, it was fully 2880 feet at Amsteg on the Ruess, just over 2000 feet at Brieg in the Rhone Valley, about 1000 feet at Guttanen in the Aare Valley, about 1550 feet above Zermatt, and 1100 feet above Saas Grund.

† My own studies of mountain districts have led me to infer that on slopes of low grade the action of snow is preservative rather than destructive. That conclusion was confirmed by Professor Garwood in a communication to the Royal Geographical Society on June 20 of the present year.

The comparatively level trough, which so often forms the uppermost part of one of the great passes across the watershed of the Alps, can hardly be explained without admitting that in each case the original watershed has been destroyed by the more rapid recession of the head of the southern valley, and this work bears every sign of having been accomplished in pre-glacial times. Sapping and plucking must have operated on a gigantic scale to separate the Viso from the Cottian watershed, to isolate the huge pyramid of the Matterhorn, with its western spur, or to make, by the recession of the Val Macugnaga, that great gap between the Strahlhorn and Monte Rosa. Some sceptics even go so far as to doubt whether the dominant forms of a non-glaciated region differ very materially from those of one which has been half-buried in snow-fields and glaciers. To my eyes, the general outlines of the mountains about the lake of Gennesaret and the northern part of the Dead Sea recalled those around the Lake of Annecy and on the south-eastern shore of Leman. The sandstone crags, which rise here and there like ruined castles from the lower plateau of the Saxon Switzerland, resembled in outline, though on a smaller scale, some of the Dolomites in the Southern Tyrol. The Lofoten Islands illustrate a half-drowned mountain range from which the glaciers have disappeared. Those were born among splintered peaks and ridges, which, though less lofty, rival in form the Aiguilles of Chamonix, and the valleys become more and more ice-worn as they descend, till the coast is fringed with skerries, every one of which is a *roche moutonnée*. The *névé* in each of these valleys has been comparatively ineffective; the ice has gathered strength with the growth of the glacier. As can be seen from photographs, the scenery of the heart of the Caucasus or of the Himalayas differs in scale rather than in kind from that of the Alps. Thus the amount of abrasion varies, other things being equal, with the latitude. The grinding away of ridges and spurs, the smoothing of the walls of troughs,* is greater in Norway than in the Alps; it is still greater in Greenland than in Norway, and it is greatest of all in the Antarctic, according to the reports of the expeditions led by Scott and Shackleton. But even in Polar regions, under the most favourable conditions, the dominant outlines of the mountains, as shown in the numerous photographs taken by both parties, and in Dr. Wilson's admirable drawings, differ in degree rather than in kind from those of mid-European ranges. It has been asserted that the parallel sides of the larger Alpine valleys—such as the Rhone above Martigny, the Lütschine near Lauterbrunnen, and the Val Bedretto below Airolo—prove that they have been made by the ice-plough rather than by running water; but in the first I am unable to discern more than the normal effects of a rather rapid river which has followed a trough of comparatively soft rocks; in the second, only the cliffs marking the channel cut by a similar stream through massive limestones—cliffs like those which elsewhere rise up the mountain flanks far above the levels reached by glaciers; while in the third I have failed to discover, after repeated examination, anything abnormal.

Many lake basins have been ascribed to the erosive action of glaciers. Since the late Sir A. Ramsay advanced this hypothesis numbers of lakes in various countries have been carefully investigated and the results published, the most recent of which is the splendid work on the Scottish lochs by Sir J. Murray and Mr. L. Pullar ("Bathymetrical Survey of the Scottish Freshwater Lochs," 1910). A contribution to science of the highest value, it has also a deeply pathetic interest, for it is a father's memorial to a much-loved son, F. P. Pullar, who, after taking a most active part in beginning the investigation, lost his life while saving others from drowning. As the time at my command is limited, and many are acquainted with the literature of the subject, I may be excused from saying more than that even these latest researches have not driven me from the position which I have maintained from the first—namely,

* If one may judge from photographs, the smoothing of the flanks of a valley is unusually conspicuous in Milton Sound, New Zealand.

that while many tarns in corries and lakelets in other favourable situations are probably due to excavation by ice, as in the mountainous districts of Britain, in Scandinavia, or in the higher parts of the Alps, the difficulty of invoking this agency increases with the size of the basin—as, for example, in the case of Loch Maree or the Lake of Annecy—till it becomes insuperable. Even if Glas Llyn and Llyn Llydaw were the work of a glacier, the rock basins of Gennesaret and the Dead Sea, still more those of the great lakes in North America and in Central Africa, must be assigned to other causes.

I pass on, therefore, to mention another difficulty in this hypothesis—that the Alpine valleys were greatly deepened during the Glacial Epoch—which has not yet, I think, received sufficient attention. From three to four hundred thousand years have elapsed, according to Penck and Brückner, since the first great advance of the Alpine ice. One of the latest estimates of the thickness of the several geological formations assigns 4000 feet* to the Pleistocene and Recent, 13,000 to the Pliocene, and 14,000 to the Miocene. If we assume the times of deposit to be proportional to the thicknesses, and adopt the larger figure for the first-named period, the duration of the Pliocene would be 1,300,000 years, and of the Miocene 1,400,000 years. To estimate the total vertical thickness of rock which has been removed from the Alps by denudation is far from easy, but I think 14,000 feet would be a liberal allowance, of which about one-seventh is assigned to the Ice Age. But during that age, according to a curve given by Penck and Brückner, the temperature was below its present amount for rather less than half (0·47) the time. Hence it follows that, since the sculpture of the Alps must have begun at least as far back as the Miocene period, one-seventh of the work has been done by ice in not quite one-fifteenth of the time, or its action must be very potent. Such data as are at our command make it probable that a Norway glacier at the present day lowers its basin by only about eighty millimetres in 1000 years; a Greenland glacier may remove some 421 millimetres in the same time, while the Vatnajökul in Iceland attains to 647 millimetres. If Alpine glaciers had been as effective as the last-named, they would not have removed, during their 188,000 years of occupation of the Alpine valleys, more than 121·6 metres, or just over 397 feet; and as this is not half the amount demanded by the more moderate advocates of erosion, we must either ascribe an abnormal activity to the vanished Alpine glaciers, or admit that water was much more effective as an excavator.

We must not forget that glaciers cannot have been important agents in the sculpture of the Alps during more than part of Pleistocene times. That sculpture probably began in the Oligocene period; for rather early in the next one the great masses of conglomerate, called *Nagelfluh*, show that powerful rivers had already carved for themselves valleys corresponding generally with and nearly as deep as those still in existence. Temperature during much of the Miocene period was not less than 12° F. above its present average. This would place the snow-line at about 12,000 feet.† In that case, if we assume the altitudes unchanged, not a snowfield would be left between the Simplon and the Maloja, the glaciers of the Pennines would shrivel into insignificance, Monte Rosa would exchange its drapery of ice for little more than a tippet of frozen snow. As the temperature fell the white robes would steal down the mountain-sides, the glaciers grow, the torrents be swollen during all the warmer months, and the work of sculpture increase in activity. Yet with a temperature even 6° higher than it now is, as it might well be at the beginning of the Pliocene period, the snow-line would be at 10,000 feet; numbers of glaciers would have disappeared, and those around the Jungfrau and the Finster Aarhorn would be hardly more important than they now are in the Western Oberland.

But denudation would begin so soon as the ground rose above the sea. Water, which cannot run off the sand exposed by the retreating tide without carving a miniature system of valleys, would never leave the nascent range intact. The Miocene Alps, even before a patch of snow could remain through the summer months, would be carved into glens and valleys. Towards the end of that period the Alps were affected by a new set of movements, which produced their most marked effects in the northern zone from the Inn to the Durance. The Oberland rose to greater importance; Mont Blanc attained its primacy; the *massif* of Dauphiné was probably developed. That, and still more the falling temperature, would increase the snowfields, glaciers, and torrents. The first would be, in the main, protective; the second, locally abrasive; the third, for the greater part of their course, erosive. No sooner had the drainage system been developed on both sides of the Alps than the valleys on the Italian side (unless we assume a very different distribution of rainfall) would work backwards more rapidly than those on the northern. Cases of trespass, such as that recorded by the long level trough on the north side of the Maloja Kulm and the precipitous descent on the southern, would become frequent. In the interglacial episodes—three in number, according to Penck and Brückner, and occupying rather more than half the epoch—the snow and ice would dwindle to something like its present amount, so that the water would resume its work. Thus I think it far more probable that the V-like portions of the Alpine valleys were in the main excavated during Pliocene ages, their upper and more open parts being largely the results of Miocene and yet earlier sculpture.

During the great advances of the ice, four in number, according to Penck and Brückner,* when the Rhone glacier covered the lowlands of Vaud and Geneva, welling on one occasion over the gaps in the Jura, and leaving its erratics in the neighbourhood of Lyons, it ought to have given signs of its erosive no less than of its transporting power. But what are the facts? In these lowlands we can see where the ice has passed over the Molasse (a Miocene sandstone); but here, instead of having crushed, torn, and uprooted the comparatively soft rock, it has produced hardly any effect. The huge glacier from the Linth Valley crept for not a few miles over a floor of stratified gravels, on which, some eight miles below Zurich, one of its moraines, formed during the last retreat, can be seen resting, without having produced more than a slight superficial disturbance. We are asked to credit glaciers with the erosion of deep valleys and the excavation of great lakes, and yet, wherever we pass from hypotheses to facts, we find them to have been singularly inefficient workmen!

I have dwelt at considerable, some may think undue, length on the Alps, because we are sure that this region from before the close of the Miocene period has been above the sea-level. It accordingly demonstrates what effects ice can produce when working on land.

In America also, to which I must now make only a passing reference, great ice-sheets formerly existed; one occupying the district west of the Rocky Mountains, another spreading from that on the north-west of Hudson's Bay, and a third from the Laurentian hill-country. These two became confluent, and their united ice-flow covered the region of the Great Lakes, halting near the eastern coast a little south of New York, but in Ohio, Indiana, and Illinois occasionally leaving moraines only a little north of the 39th parallel of latitude.† Of these relics my first-hand knowledge is very small, but the admirably illustrated

* I have doubts whether this is not too great.

† I take the fall of temperature for a rise in altitude as 1° F. for 300 feet or, when the differences in the latter are large, 3° per 1000 feet. These estimates will, I think, be sufficiently accurate. The figures given by Hann (see for a discussion of the question, *Report of British Association*, 1909, p. 93) work out to 1° F. for each 318 feet of ascent up to about 10,000 feet).

* On the exact number I have not had the opportunity of forming an opinion.

† Some of the glacial drifts on the eastern side of the continent, as we shall find, may have been deposited in the sea.

reports and other writings of American geologists* indicate that, if we make due allowance for the differences in environment, the tills and associated deposits on their continent are similar in character to those of the Alps.†

In our own country and in corresponding parts of Northern Europe we must take into account the possible co-operation of the sea. In these, however, geologists agree that, for at least a portion of the Ice Age, glaciers occupied the mountain districts. Here ice-worn rocks, moraines and perched blocks, tarns in corries, and perhaps lakelets in valleys, demonstrate the former presence of a mantle of snow and ice. Glaciers radiated outwards from more than one focus in Ireland, Scotland, the English Lake District, and Wales, and trespassed, at the time of their greatest development upon the adjacent lowlands. They are generally believed to have advanced and retreated more than once, and their movements have been correlated by Prof. J. Geikie with those already mentioned in the Alps. Into that very difficult question I must not enter; for my present purpose it is enough to say that in early Pleistocene times glaciers undoubtedly existed in the mountain districts of Britain and even formed piedmont ice-sheets on the lowlands. On the west side of England, smoothed and striated rocks have been observed near Liverpool, which can hardly be due to the movements of shore-ice, and at Little Crosby a considerable surface has been cleared from the overlying boulder clay by the exertions of the late Mr. T. M. Reade and his son, Mr. A. Lyall Reade. But, so far as I am aware, rocks thus affected have not yet been discovered in the Wirral peninsula. On the eastern side of England similar markings have been found down to the coast of Durham, but a more southern extension of land ice cannot be taken for granted. In this direction, however, so far as the tidal valley of the Thames, and in corresponding parts of the central and western lowlands, certain deposits occur which, though to a great extent of glacial origin, are in many respects different from those left by land ice in the Alpine regions and in Northern America.

They present us with problems the nature of which may be inferred from a brief statement of the facts. On the Norfolk coast we find the glacial drifts resting, sometimes on the chalk, sometimes on strata of very late Pliocene or early Pleistocene age. The latter show that in their time the strand-line must have oscillated slightly on either side of its present level. The earliest of the glacial deposits, called the Cromer Till and Contorted Drift, presents its most remarkable development in the cliffs on either side of that town. Here it consists of boulder clays and alternating beds of sand and clay; the first-named, two or three in number, somewhat limited in extent, and rather lenticular in form, are slightly sandy clays, full of pieces of chalk, flint, and other kinds of rock, some of the last having travelled from long distances. Yet more remarkable are the huge erratics of chalk in the neighbourhood of which the sands and clays exhibit extraordinary contortions. Like the beds of till, they have not been found very far inland, for there the group appears as a whole to be represented by a stony loam, resembling a mixture of the sandy and clayey material, and this is restricted to a zone some twenty miles wide, bordering the coast of Norfolk and Suffolk; not extending south of the latter county, but being probably represented to the north of the Humber. Above these is a group of false-bedded sands and gravels, variable in thickness and character—the Mid-glacial Sands of Searles V. Wood and F. W. Harmer. They extend over a wider area, and may be traced, according to some geologists, nearly to the western side of England, rising in that direction to a greater height above sea-level. But as it is impossible to prove that all isolated patches of these materials are identical in age, we can only be certain that some of them are older than the next deposit, a boulder clay, which extends over a large part of the lowlands in the Eastern Counties. This has a general resemblance to the Cromer Till, but its matrix is rather more clayey and is variable in colour. In and north of Yorkshire, as well as on the seaward side of the Lincolnshire wolds, it is generally brownish or purplish, but on their western side and as far as the clay goes to the south it is some shade of grey. Near to these wolds, in mid-Norfolk, and on the northern margin of Suffolk, it has a whitish tint, owing to the abundance of comminuted chalk. To the south and west of this area it is dark, from the similar presence of Kimeridge clay. Yet further west it assumes an intermediate colour by having drawn upon the Oxford clay. This boulder clay, whether the chalky or the purple, in which partings of sand sometimes occur, must once have covered, according to Mr. F. W. Harmer, an area about ten thousand square miles in extent. It spreads like a coverlet over the pre-glacial irregularities of the surface. It caps the hills, attaining sometimes an elevation of fully 500 feet above sea-level;* it fills up valleys,† sometimes partly, sometimes wholly, the original floors of which occasionally lie more than 100 feet below the same level. This boulder clay, often with an underlying sand or gravel, extends to the south as far as the neighbourhood of Muswell Hill and Finchley; hence its margin runs westward through Buckinghamshire, and then, bending northwards, passes to the west of Coventry. On this side of the Pennine Chain the matrix of the boulder clay is again reddish, being mainly derived from the sands and marls of the Trias; pieces of chalk and flint are rare (no doubt coming from Antrim), though other rocks are often plentiful enough. Some authorities are of opinion that the drift in most parts of Lancashire and Cheshire is separable, as on the eastern coasts, into a lower and an upper boulder clay, with intervening gravelly sands, but others think that the association of the first and third is lenticular rather than successive. Here also the lower clay cannot be traced very far inland, eastward, or southward; the others have a wider extension, but they reach a greater elevation above sea-level than on the eastern side of England. The sand is inconstant in thickness, being sometimes hardly represented, sometimes as much as 200 feet. The upper clay runs on its more eastern side up to the chalky boulder clay, and extends on the south at least into Worcestershire. On the western side it merges with the upper member of the drifts radiating from the mountains of North Wales, which often exhibit a similar tripartite division, while (as we learn from the officers of the Geological Survey) boulder clays and gravelly sands, which it must suffice to mention, extend from the highlands of South Wales for a considerable distance to the south-east and south. Boulder clay has not been recognised in Devon or Cornwall, though occasional erratics are found which seem to demand some form of ice-transport. A limited deposit, however, of that clay, containing boulders now and then over a yard in diameter, occurs near Selsey Bill on the Sussex coast, which most geologists consider to have been formed by floating rather than by land ice.

Marine shells are not very infrequent in the lower clays of East Anglia and Yorkshire, but are commonly broken. The well-known Bridlington Crag is the most conspicuous instance, but this is explained by many geologists as an erratic—a piece of an ancient North Sea bed caught up and transported, like the other molluscs, by an advancing ice-

* See the *Reports of the United States Geological Survey* (from vol. iii. onwards), *Journal of Geology*, *American Journal of Science*, and local publications too numerous to mention. Among these the studies in Greenland by Prof. Chamberlain are especially valuable for the light they throw on the movement of large glaciers and the transport of *débris* in the lower part of the ice.

† Here, however, we cannot always be so sure of the absence of the sea.

* Not far from Royston it is found at a height of 525 feet above O.D. See F. W. Harmer, *Pleistocene Period in the Eastern Counties*, p. 115.

† At Old North Road Station, on a tributary of the Cam, the boulder clay was pierced to a depth of 180 feet, and at Impington it goes to 60 feet below sea-level. Near Hitchin, a hidden valley, traced for seven or eight miles, was proved to a depth of 68 feet below O.D., and one near Newport in Essex, to 140 feet. Depths were also found of 120 feet at West Horseheath in Suffolk, of 120 feet on low ground two miles S.W. of Sandy in Bedfordshire, of from 100 to 160 feet below the sea at Fossdyke, Long Sutton, and Boston, and at Glemsford in the valley of the Stour, 477 feet of drift was passed through before reaching the chalk. See F. W. Harmer, *Quart. Journ. Geol. Soc.*, 1907, lxiii., 494).

sneet. They also claim a derivative origin for the organic contents of the overlying sands and gravels, but some authorities consider the majority to be contemporaneous. Near the western coast of England, shells in much the same state of preservation as those on the present shore are far from rare in the lower clay, where they are associated with numerous striated stones, often closely resembling those which have travelled beneath a glacier, both from the Lake District and the less distant Trias. Shells are also found in the overlying sands up the valleys of the Dee and Severn, at occasional localities, even as far inland as Bridgnorth, the heights of the deposits varying from about 120 feet to over 500 feet above the sea-level. If we also take account of the upper boulder clay, where it can be distinguished, the list of marine molluscs, ostracods, and foraminifers from these western drifts is a rather long one (W. Shone, *Quart. Journ. Geol. Soc.*, 1878, xxxiv., p. 383).

Marine shells, however, on the western side of England, are not restricted to the lowlands. Three instances, all occurring over 1000 feet above sea-level, claim more than a passing mention. At Macclesfield, almost thirty miles in a straight line from the head of the estuary of the Mersey, boulder clays associated with stratified gravels and sands have been described by several observers.* The clay stops at about 1000 feet, but the sands and gravels go on to nearly 1300 feet, while isolated erratics are found up to about 100 feet higher. Sea shells, some of which are in good condition, have been obtained at various elevations, the highest being about 1200 feet above sea-level. About forty-eight species of molluscs have been recognised, and the fauna, with a few exceptions, more arctic in character and now found at a greater depth, is one which at the present day lives in a temperate climate at a depth of a few fathoms.

The shell-bearing gravels at Gloppa, near Oswestry, which are about thirty miles from the head of the Dee estuary, were carefully described in 1892 by Mr. A. C. Nicholson. He has enumerated fully sixty species, of which, however, many are rare. As his collection† shows, the bivalves are generally broken, but a fair number of the univalves are tolerably perfect. The deposit itself consists of alternating seams of sand and gravel, the one generally about an inch in thickness, the other varying from a few inches to a foot. The difference in the amount of rounding shown by the stones is a noteworthy feature. They are not seldom striated; some have come from Scotland, others from the Lake District, but the majority from Wales, the last being the more angular. Here and there a block, sometimes exceeding a foot in diameter and usually from the last-named country, has been dropped among the smaller material, most of which ranges in diameter from half-an-inch to an inch and a-half. The beds in one or two places show contortions; but as a rule, though slightly wavy and with a gentle dip rather to the west of south, they are uniformly deposited. In this respect, and in the unequal wearing of the materials, the Gloppa deposit differs from most gravels that I have seen. Its situation also is peculiar. It is on the flattened top of a rocky spur from higher hills, which falls rather steeply to the Shropshire lowland on the eastern side, and on the more western is defined by a small valley which enlarges gradually as it descends towards the Severn. If the country were gradually depressed for nearly 1200 feet, this upland would become, first a promontory, then an island, and finally a shoal.

The third instance, on Moel Tryfaen in Carnarvonshire, was carefully investigated and described by a Committee of this Association about ten years ago (*Brit. Assoc. Report*, 1899, pp. 414—423). The shells occur in an irregularly stratified sand and gravel, resting on slate, and overlain by a boulder clay, no great distance from and a few dozen feet below the rocky summit of the hill, being about 130 feet above the level of the sea and at least five miles from its margin. About fifty-five species of molluscs and twenty-three of foraminifers have been identified. According to the late Dr. J. Gwyn Jeffreys (*Quart. Journ. Geol. Soc.*, 1880, xxxvi., p. 355) the majority of the molluscs are littoral in habit, the rest such as live in from ten to twenty fathoms of water. Most of the erratics have been derived from the Welsh mountains, but some rocks from Anglesey have also been obtained, and a few pebbles of Lake District and Scotch rocks. If the sea were about 1300 feet above its present level, Moel Tryfaen would become a small rocky island, open to the storms from the west and north, and nearly a mile and a half away from the nearest land.

I must pass more rapidly over Ireland. The signs of vanished glaciers—ice-worn rocks and characteristic boulder-clays—are numerous, and may be traced in places down to the sea-level, but the principal outflow of the ice, according to some competent observers, was from a comparatively low district, extending diagonally across the island from the south of Lough Neagh to north of Galway Bay. Glaciers, however, must have first begun to form in the mountains on the northern and southern side of this zone, and we should have expected that, whatever might happen on the lowlands, they would continue to assert themselves. In no other part of the British Islands are eskers, which some geologists think were formed when a glacier reached the sea, so strikingly developed. Here also an upper and a lower boulder-clay, the former being the more sparsely distributed, are often divided by a wide-spread group of sands and gravels, which locally, as in Great Britain, contains, sometimes abundantly, shells and other marine organisms; more than twenty species of molluscs, with foraminifers, a barnacle, and perforations of annelids, having been described. These are found in counties Dublin and Wicklow, at various altitudes,* from a little above sea-level to a height of 1300 feet.

Not the least perplexing of the glacial phenomena in the British Isles is the distribution of erratics, which has been already mentioned in passing. On the Norfolk coast, masses of chalk, often thousands of cubic feet in volume, occur in the lowest member of the glacial series, with occasional great blocks of sand and gravel, which must have once been frozen. But these, or at any rate the larger of them, have no doubt been derived from the immediate neighbourhood. Huge erratics also occasionally occur in the upper boulder clay—sometimes of chalk, as at Roslyn Hill near Ely and at Ridlington in Rutland, of jurassic limestone, near Great Ponton, to the south of Grantham, and of Lower Kimeridge clay near Biggleswade (H. Home, *Quart. Journ. Geol. Soc.*, 1903, lix., p. 375). These also probably have not travelled more than a few miles. But others of smaller size have often made much longer journeys. The boulder clays of Eastern England are full of pieces of rock, commonly ranging from about half an inch to a foot in diameter. Among these are samples of the carboniferous, jurassic, and cretaceous rocks of Yorkshire and the adjacent counties; the red chalk from either Hunstanton, Speeton, or some part of the Lincolnshire wolds, being found as far south as the northern heights of London. Even the chalk and flint, the former of which, especially in the upper boulder clay, commonly occurs in well-worn pebbles, are frequently not the local but the northern varieties. And with these are mingled specimens from yet more distant sources — Cheviot porphyrites, South Scotch basalts, even some of the crystalline rocks of the Highlands. Whatever was the transporting agent, its general direction was southerly, with a slight deflection towards the east in the last-named cases.

But the path of these erratics has been crossed by two streams, one coming from the west, the other from the east. On the western side of the Pennine watershed the Shap granite rises at Wasdale Crag to a height of about 1600 feet above sea-level. Boulders from it have descended

* *Memoirs of the Geological Survey*: "Country around Macclesfield," T. I. Pocock, 1906, p. 85. For some notes on Moel Tryfaen and the altitudes of other localities at which marine organisms have been found see J. Gwyn Jeffreys, *Quart. Journ. Geol. Soc.*, 1880, xxxvi., p. 351. For the occurrence of such remains in the Vale of Clwyd see a paper by T. McK. Hughes in *Proc. Chester Soc. of Nat. Hist.*, 1884.

† Now deposited in the Oswestry Museum.

* See T. M. Reade, *Proc. Liverpool Geol. Soc.*, 1893-94, p. 183, for some weighty arguments in favour of a marine origin for these deposits.

the Eden valley to beyond Penrith; they have travelled in the opposite direction almost to Lancaster,* and a large number of them have actually made their way near the line of the Lake District watershed, across the upper valley of the Eden, and over the high pass of Stainmoor Forest,† whence they descended into Upper Teesdale. Subsequently the stream seems to have bifurcated, one part passing straight out to the present sea-bed, by way of the lower course of the Tees, to be afterwards driven back on to the Yorkshire coast. The other part crossed the low watershed between the Tees and the Ouse, descended the Vale of York, and spread widely over the plain.‡ Shap boulders by some means penetrated into the valleys tributary to the Ouse on its west bank, and they have been observed as far to the south-east as Royston, near Barnsley. It is noteworthy that Lake District rocks have been occasionally recorded from Airedale and even the neighbourhood of Colne, though the granite from Shap has not been found there. The other stream started from Scandinavia. Erratics, some of which must have come from the north-western side of the Christiania Fjord, occur on or near the coast from Essex to Yorkshire, and occasionally even as far north as Aberdeen, while they have been traced from the East Anglian coast to near Ware, Hitchin, and Bedford (R. H. Rastall and J. Romanes, *Quart. Journ. Geol. Soc.*, 1909, lxv., p. 246). It may be important to notice that these Scandinavian erratics are often waterworn, like those dispersed over Denmark and parts of Northern Germany.

On the western side of England the course of erratics is not less remarkable. Boulders from South-Western Scotland, especially from the Kirkcudbright district, both waterworn and angular, are scattered over the lowlands as far south as Wolverhampton, Bridgnorth, and Church Stretton. They may be traced along the border of North Wales, occurring, as has been said, though generally small, up to about 1300 feet on Moel Tryfaen, 1100 feet at Gloppa, and more than that height on the hills east of Macclesfield. Boulders from the Lake District are scattered over much the same area and attain the same elevation, but extend, as might be expected, rather farther to the east in Lancashire. They also have been found on the eastern side of the Pennine watershed, perhaps the most remarkable instances being in the dales of the Derbyshire Derwent and on the adjacent hills as much as 1400 feet above the sea-level.§ A third remarkable stream of erratics from the neighbourhood of the Arenig mountains extends from near the estuary of the Dee right across the paths of the two streams from the north, its eastern border passing near Rugeley, Birmingham, and Bromsgrove. They also range high, occurring almost 900 feet above sea-level on Romsley Hill, north of the Clents, and being common at Gloppa. Boulders also from the basalt mass of Rowley Regis have travelled in some cases between four and five miles, and in directions ranging from rather west of south to north-east; and, though that mass hardly rises above the 700-feet contour line, one lies with an Arenig boulder on Romsley Hill. From Charnwood Forest, the crags of which range up to about 850 feet above sea-level, boulders have started which have been traced over an area to the south and west to a distance of more than twenty miles.

Such, then, are the facts, which call for an interpretation, More than one has been proposed; but it will be well, before discussing them, to arrive at some idea of the climate of these islands during the colder part of the Glacial Epoch. Unless that were associated with very great changes in the distribution of sea and land in Northern and North-Western Europe, we may assume that neither the relative position of the isotherms nor the distribution of precipitation would be very materially altered. A general fall of temperature in the northern hemisphere might so weaken the warmer ocean current from the south-west that our coasts might be approached by a cold one from the opposite direction.* But though these changes might diminish the difference between the temperatures of London and Leipzig, they would not make the former colder than the latter. At the present day the snow-line in the Alps on either side of the Upper Rhone Valley is not far from 8000 feet above sea-level, and this corresponds with a temperature of about 30°. Glaciers, however, are not generally formed till about 1000 feet higher, where the temperature is approximately 27°. Penck and Brückner place this line during the coldest part of the Ice Age at about 4000 feet.† In that case the temperature of the Swiss lowland would be some 15° lower than now, or near the freezing-point.‡ If this fall were general, it would bring back the small glaciers on the Gran Sasso d'Italia and Monte Rotondo in Corsica; perhaps also among the higher parts of the Vosges and Schwarzwald.§ In our own country it would give a temperature of about 35° at Carnarvon, and 23° on the top of Snowdon, of 32° at Fort William, and 17·5° on the top of Ben Nevis. If, in addition to this, the land were 600 feet higher than now (as it probably was, at any rate in the beginning of the Glacial Epoch), there would be a further drop of 2°, so that glaciers would form in the corries of Snowdon, and the region round Ben Nevis might resemble the Oetzthal Alps at the present day. This change of itself would be insufficient, and any larger drop in the ocean-level would have to be continental in its effects, since we cannot assume a local upheaval of much more than the above amount without seriously interfering with the river system of North Central Europe. But these changes, especially the former, might indirectly diminish the abnormal warmth of winter on our north-western coasts.‖ It is difficult to estimate the effect of this. If it did no more than place Carnarvon on the isotherm of Berlin (now lower by 2°), that would hardly bring a glacier from the Snowdonian region down to the sea. At the present time London is about 18° warmer than a place in the same latitude near the Labrador coast or the mouth of the Amur River, but the removal of that difference would involve greater changes in the distribution of sea and land than seems possible at an epoch comparatively speaking so recent. I am doubtful whether we can attribute to changed currents a reduction in British temperatures of so much as 11°; but, if we did, this would amount to 28° from all causes, and give a temperature of 20° to 22° at sea-level in England, during the coldest part of the Glacial Epoch.¶ That is now found, roughly speaking, in Spitzbergen, which, since its mountains rise to much the same height, should give us a general idea of the condition of Britain in the olden time.

What would then be the state of Scandinavia? Its present temperature ranges on the west coast from about 45° in the south to 35° in the north.** But this region must

* A pebble of it is said to have been identified at Moel Tryfaen.

† The lowest part of the gap is about 1400 feet. A little to the south is another gap about 200 feet lower, but none of the boulders seem to have taken that route.

‡ A boulder was even found above Grosmont in the Eske valley, 345 feet above sea-level.

§ Communication from Dr. H. Arnold-Bemrose.

* Facts relating to this subject will be found in "Climate and Time," by J. Croll, 1875, ch. ii. and iii. Of course the air currents would also be affected, and perhaps diminish precipitation as the latitude increased.

† *Loc. cit.*, p. 586, *et seq.* They say the snow-line, which would mean that the temperature was only 12° lower than now; but as possibly this line might then more nearly correspond with that of glacier formation, I will provisionally accept the higher figures, especially since Corsica, the Apennines, and some other localities in Europe, seem to require a reduction of rather more than 12°.

‡ It would be 32·5° at Zurich, 31·6° at Bern, 34·1° at Geneva, about 39·0° on the plain of Piedmont, and 36·0° at Lyons.

§ See for particulars the author's "Ice Work" ("International Scientific Series") p. 237.

‖ For much valuable information on these questions see a paper on the "Climate of the Pleistocene Epoch" (F. W. Harmer, *Quart. journ. Geol. Soc.*, 1901, lvii., p. 405).

¶ The present temperature in Ireland over the zone (from S. of Belfast to N. of Galway Bay) which is supposed to have formed the divide of the central snowfield may be given as from 49° to 50°, nearly the same as at the sea-level in Carnarvonshire. Thus, though the district is less mountainous than Wales, it would not need a greater reduction, for the snowfall would probably be rather larger. But this reduction could hardly be less than 20°, for the glaciers would have to form nearly at the present sea-level.

** It is 44·42° at Bergen, 38·48° at Bodo, 35·42° at Hammerfest, 41·36° at Christiania and Stockholm.

now be very much, possibly 1800 feet, lower than it was in pre-glacial, perhaps also in part of glacial, times.* If we add 5° for this to the original 15°, and allowed so much as 18° for the diversion of the warm current, the temperature of Scandinavia would range from 7° to −3°, approximately that of Greenland northwards from Upernivik. But since the difference at the present day between Cape Farewell and Christiania (the one in an abnormally cold region, the other in one correspondingly warm) is only 7°, that allowance seems much too large, while without it Scandinavia would correspond in temperature with some part of that country from south of Upernivik to north of Frederikshaab.† But if Christiania were not colder than Jakobshavn is now, or Britain than Spitzbergen, we are precluded from comparisons with the coasts of Baffin Bay or Victoria Land.

Thus the ice-sheet from Scandinavia would probably be much greater than those generated in Britain. It would, however, find an obstacle to progress westwards, which cannot be ignored. If the bed of the North Sea became dry land, owing to a general rise of 600 feet, that would still be separated from Norway by a deep channel, extending from the Christiania Fjord round the coast northward. Even then this would be everywhere more than another 600 feet deep, and almost as wide as the Straits of Dover (for details see *Geol. Mag.*, 1899, pp. 97 and 282). The ice must cross this and afterwards be forced for more than 300 miles up a slope, which, though gentle, would be in vertical height at least 600 feet. The task, if accomplished by thrust from behind, would be a heavy one, and, so far as I know, without a parallel at the present day; if the viscosity of the ice enabled it to flow, as has lately been urged (H. M. Deeley, *Geol. Mag.*, 1909, p. 239), we must be cautious in appealing to the great Antarctic barrier, because we now learn that more than half of it is only consolidated snow (E. Shackleton, "The Heart of the Antarctic," ii., 277). Moreover, if the ice floated across that channel, the thickness of the boulder-bearing layers would be diminished by melting (as in Ross's Barrier), and the more viscous the material, the greater the tendency for these to be left behind by the overflow of the cleaner upper layers. If, however, the whole region became dry land, the Scandinavian glaciers would descend into a broad valley, considerably more than 1200 feet deep, which would afford them an easy path to the Arctic Ocean, so that only a lateral overflow, inconsiderable in volume, could spread itself over the western plateau.‡ An attempt to escape this difficulty has been made by assuming the existence of an independent centre of distribution for ice and boulders near the middle of the North Sea bed—which would demand rather exceptional conditions of temperature and precipitation—(*Geol. Mag.*, 1901, pp. 142, 187, 284, 332); but in such case either the Scandinavian ice would be fended off from England, or the boulders, prior to its advance, must have been dropped by floating ice on the neighbouring sea-floor.

If, then, our own country were but little better than Spitzbergen as a producer of ice, and Scandinavia only surpassed Southern Greenland in having a rather heavier snowfall, what interpretation may we give to the glacial phenomena of Britain? Three have been proposed. One asserts that throughout the Glacial Epoch the British Isles generally stood at a higher level, so that the ice which almost buried them flowed out on to the beds of the North and Irish Seas. The boulder clays represent its moraines. The stratified sands and gravels were deposited in lakes formed by the rivers which were dammed up by ice-sheets.* A second interpretation recognises the presence of glaciers in the mountain regions, but maintains that the land, at the outset rather above its present level, gradually sank beneath the sea, till the depth of water over the eastern coast of England was fully 500 feet, and over the western nearly 1400 feet, from which depression it slowly recovered. By any such submergence Great Britain and Ireland would be broken up into a cluster of hilly islands, between which the tide from an extended Atlantic would sweep eastwards twice a day, its currents running strong through the narrower sounds, while movements in the reverse direction at the ebb would be much less vigorous. The third interpretation, in some respects intermediate, was first advanced by the late Professor Carvill Lewis, who held that the peculiar boulder clays and associated sands (such as those of East Anglia), which, as was then thought, were not found more than about 450 feet above the present sea-level, had been deposited in a great fresh-water lake, held up by the ice-sheets already mentioned and by an isthmus, which at that time occupied the place of the Straits of Dover. Thus, these deposits, though indirectly due to land-ice, were actually fluviatile or lacustrine. But this interpretation need not detain us, though the former existence of such lakes is still maintained, on a small scale in Britain, on a much larger one in North America, because, as was pointed out when it was first advanced, it fails to explain the numerous erratic blocks and shell-bearing sands which occur far above the margin of the hypothetical lake.

Each of the other two hypotheses involves grave difficulties. That of great confluent ice-sheets creeping over the British lowlands demands, as has been intimated, climatal conditions which are scarcely possible, and makes it hard to explain the sands and gravels, sometimes with regular alternate bedding, but more generally indicative of strong current action, which occur at various elevations to over 1300 feet above sea-level, and seem too widespread to have been formed either beneath an ice-sheet or in lakes held up by one; for the latter, if of any size, would speedily check the velocity of influent streams. Also the mixture and crossing of boulders, which we have described, are inexplicable without the most extraordinary oscillations in the size of the contributing glaciers. To suppose that the Scandinavian ice reached to Bedfordshire and Herts and then retired in favour of North British glaciers, or *vice versâ*, assumes an amount of variation which, so far as I am aware, is without a parallel elsewhere. So also the mixture of boulders from South Scotland, the Lake District, and North Wales which lie, especially in parts of Staffordshire and Shropshire, as if dropped upon the surface, far exceeds what may reasonably be attributed to variations amplified by lateral spreading of mountain glaciers on reaching a lowland, while the frequent presence of shells in the drifts, dozens of miles away from the present coast, implies a rather improbable scooping up of the sea-bed without much injury to such fragile objects. The ice also must have been curiously inconstant in its operations. It is supposed in one place to have glided gently over its bed, in another to have gripped and torn out huge masses of rock.† Both actions may be possible in a mountain region, but it is very difficult to understand how they could occur in a lowland or plain. Besides this we can only account for some singular aberrations of boulders, such as Shap granite well above Grosmont in Eskdale, or the Scandinavian rhomb-porphyry above

* For particulars see *Geol. Mag.*, 1899, p. 97 (W. H. Hudleston), and p. 282 (T. G. Bonney).

† Christiania and Cape Farewell (Greenland) are nearly on the same latitude.

‡ It has indeed been affirmed (Brögger, "Om de Senglaciale og Postglaciale Nivaforandringer i Kristianiafelted," p. 682) that at the time of the great ice-sheet of Europe the sea-bottom must have been uplifted at least 8500 feet higher than at present. This may be a ready explanation of the occurrence of certain dead shells in deep water, but, unless extremely local, it would revolutionise the drainage system of Central Europe.

* See Warren Upham, *Monogr. U.S. Geol. Survey*, 1896, xxv. This explanation commends itself to the majority of British geologists as an explanation of the noted parallel roads of Glenroy, but it is premature to speak of it as "conclusively shown" (*Quart. Journ. Geol. Soc.*, 1902, lviii., 473) until a fundamental difficulty which it presents has been discussed and removed.

† That this has occurred at Cromer is a very dubious hypothesis (see *Geol. Mag.*, 1905, pp. 307, 524) The curious relations of the drift and chalk in the islands of Möen and Rügen are sometimes supposed to prove the same action. Knowing both well, I have no hesitation in saying that the chalk there is, as a rule, as much *in situ* as it is in the Isle of Wight.

Lockwood,* near Huddersfield, by assuming a flexibility in the lobes of an ice-sheet which it is hard to match at the present time. Again, the boulder clay of the eastern counties is crowded, as we have described, with pebbles of chalk, which generally are not of local origin, but have come from north of the Wash. Whether from the bed of a river or from a sea-beach, they are certainly water-worn. But if preglacial, the supply would be quickly exhausted, so that they would usually be confined to the lower part of the clay. As it is, though perhaps they run larger here, they abound throughout. The so-called moraines near York (supposed to have been left by a glacier retreating up that vale), those in the neighbourhood of Flamborough Head and of Sheringham (regarded as relics of the North Sea ice-sheet) do not, in my opinion, show any important difference in outline from ordinary hills of sands and gravels, and their materials are wholly unlike those of any indubitable moraines that I have either seen or studied in photographs. It may be said that the British glaciers passed over very different rocks from the Alpine; but the Swiss molasse ought to have supplied abundant sand, and the older interglacial gravels quantities of pebbles; yet the differences between the morainic materials on the flank of the Jura or near the town of Geneva and those close to the foot of the Alps are varietal rather than specific.

Some authorities, however, attribute such magnitude to the ice-sheets radiating from Scandinavia that they depict them, at the time of maximum extension, as not only traversing the North Sea bed and trespassing upon the coast of England, but also radiating southward to overwhelm Denmark and Holland, to invade Northern Germany and Poland, to obliterate Hanover, Berlin, and Warsaw, and to stop but little short of Dresden and Cracow, while burying Russia on the east to within no great distance of the Volga and on the south to the neighbourhood of Kief. Their presence, however, so far as I can ascertain, is inferred from evidence† very similar to that which we have discussed in the British lowlands. That Scandinavia was at one time almost wholly buried beneath snow and ice is indubitable; it is equally so that at the outset the land stood above its present level, and that during the later stages of the Glacial Epoch parts, at any rate of Southern Norway, had sunk down to a maximum depth of 800 feet. In Germany, however, erratics are scattered over its plain and stranded on the slopes of the Harz and Riesengebirge up to about 1400 feet above sea-level. The glacial drifts of the lowlands sometimes contain dislodged masses of neighbouring rocks like those at Cromer, and we read of other indications of ice action. I must, however, observe that since the glacial deposits of Möen, Warnemünde, and Rügen often present not only close resemblances to those of our eastern counties but also very similar difficulties, it is not permissible to quote the one in support of the other, seeing that the origin of each is equally dubious. Given a sufficient "head" of ice in northern regions, it might be possible to transfer the remains of organisms from the bed of the Irish sea to Moel Tryfaen, Macclesfield, and Gloppa; but at the last-named, if not at the others, we must assume the existence of steadily alternating currents in the lakes in order to explain the corresponding bedding of the deposit. This, however, is not the only difficulty. The "Irish Sea glacier" is supposed to have been composed of streams from Ireland, South-West Scotland, and the Lake District, of which the second furnished the dominant contingent; the first-named not producing any direct effect on the western coast of Great Britain, and the third being made to feel its inferiority and "shouldered in upon the mainland." But even if this ever happened, ought not the Welsh ice to have joined issue with the invaders a good many miles to the north of its own coast?‡ Welsh boulders at any rate are common near the summit of Moel Tryfaen, and I have no hesitation in saying that the pebbles of riebeckite-rock, far from rare in its drifts, come from Mynydd Mawr, hardly half a league to the E.S.E., and not from Ailsa Craig.*

As such frequent appeal is made to the superior volume of the ice-sheet which poured from the Northern Hills over the bed of the Irish Sea, I will compare in more detail the ice-producing capacities of the several districts. The present temperature of West-Central Scotland may be taken as 47°; its surface as averaging about 2500 feet, rising occasionally to nearly 4000 feet above sea-level. In the western part of the Southern Uplands the temperature is a degree higher, and the average for altitude at most not above 1500 feet. In the Lake District and the Northern Pennines the temperature is increased by another degree, and the heights are, for the one 1800 feet with a maximum of 3162 feet, for the other 1200 feet and 2892 feet. In North Wales the temperature is 50°, the average height perhaps 2000 feet, and the culminating point 3571 feet. For the purpose of comparing the ice-producing powers of these districts we may bring them to one temperature by adding 300 feet to the height for each degree below that of the Welsh region. This would raise the average elevation of Central and Southern Scotland to 3400 feet and 2100 feet respectively; for the Lake District and Northern Pennines to 2100 feet and 1500 feet. We may picture to ourselves what this would mean, if the snow-line were at the sea-level in North Wales, by imagining 8000 feet added to its height and comparing it with the Alps. North Wales would then resemble a part of that chain which had an average height of about 10,000 feet above sea-level, and culminated in a peak of 11,571 feet; the Lake District would hardly differ from it; the Northern Pennines would be like a range of about 9000 feet, its highest peak being 11,192 feet. Southern Scotland would be much the same in average height as the first and second, and would rise, though rarely, to above 11,000 feet; the average in Central Scotland would be about 11,400 feet, and the maximum about 13,000 feet. Thus, North Wales, the Lake District, and the Southern Uplands would differ little in ice-productive power; while Central Scotland would distinctly exceed them, but not more than the group around the Finsteraarhorn does that giving birth to the Rhone glacier. In one respect, however, all these districts would differ from the Alps—that at 8000 feet, the surface, instead of being furrowed with valleys, small and great, would be a gently shelving plateau, which would favour the formation of piedmont glaciers. Still, unless we assume the present distribution of rainfall to be completely altered (for which I do not know any reason), the relative magnitudes of the ice coming from these centres (whether separate glaciers or confluent sheets) could differ but little. Scotch ice would not appreciably "shoulder inland" that from the Lake District, nor would the Welsh ice be imprisoned within its own valleys.

During the last few years, however, the lake-hypothesis of Carvill Lewis has been revived under a rather different form by some English advocates of land-ice. For instance, the former presence of ice-dammed lakes is supposed to be indicated in the upper parts of the Cleveland Hills by certain overflow channels. I may be allowed to observe that, though this view is the outcome of much acute observation and reasoning (P. F. Kendall, *Quart. Journ. Geol. Soc.*, 1902, lviii., 471), it is wholly dependent upon the ice-barriers already mentioned, and that if they dissolve

* About half-way across England and 810 feet above sea-level. P. F. Kendall, *Quart. Journ. Geol. Soc.*, 1902, lviii., p. 498

† A valuable summary of it is given in *The Great Ice Age*, J. Geikie, 1894, ch. xxix., xxx.

‡ From Moel Tryfaen to the nearest point of Scotland is well over a hundred miles, and it is a few less than this distance from Gloppa to the Lake District. In order to allow the Irish Sea ice-sheet to reach the top of Moel Tryfaen the glacier produetive power of Snowdonia has been minimised (Wright, "Man and the Glacial Epoch," p. 171). But the difference between that and the Arenig region is not great enough to make the one incompetent to protect its own borderland while the other could send an ice-sheet which could almost cover the Clent Hills and reach the neighbourhood of Birmingham. Anglesey also, if we suppose a slight elevation and a temperature of 29° at the sea-level, would become a centre of ice-distribution and an advance guard to North Wales.

* The boulders of picrite near North Nobla, from Llanerchymedd, though they have travelled southward, have moved away much to the west.

before the dry light of sceptical criticism, the lakes will "leave not a rack behind." I must also confess that to my eyes the so-called "overflow channels" much more closely resemble the remnants of ancient valley-systems, formed by only moderately rapid rivers, which have been isolated by the trespass of younger and more energetic streams, and they suggest that the main features of this picturesque upland were developed before rather than after the beginning of the Glacial Epoch. I think that even "Lake Pickering," though it has become an accepted fact with several geologists of high repute, can be more simply explained as a two-branched "valley of strike," formed on the Kimeridge clay, the eastern arm of which was beheaded, even in preglacial times, by the sea.* As to Lake Oxford (F. W. Harmer, *Quart. Journ. Geol. Soc.*, 1907, lxiii., 470), I must confess myself still more sceptical. Some changes no doubt have occurred in later glacial and postglacial times; valleys have been here raised by deposit, there deepened sometimes by as much as 100 feet; the courses of lowland rivers may occasionally have been altered; but I doubt whether, since those times began, either ice-sheet or lake has ever concealed the site of that University city.

The submergence hypothesis assumes that, at the beginning of the Glacial Epoch, our islands stood rather above their present level, and during it gradually subsided, on the west to a greater extent than on the east, till at last the movement was reversed, and they returned nearly to their former position. During most of this time glaciers came down to the sea from the more mountainous islands, and in winter an ice-foot formed upon the shore. This, on becoming detached, carried away boulders, beach pebbles, and finer detritus. Great quantities of the last also were swept by swollen streams into the estuaries, and spread over the sea-bed by coast currents, settling down especially in the quiet depths of submerged valleys. Shore ice in Arctic regions, as Colonel H. W. Feilden (*Quart. Journ. Geol. Soc.*, 1878, xxxiv., 556) has described, can striate stones and even the rock beneath it, and is able, on a subsiding area, gradually to push boulders up to a higher level. In fact, the state of the British region in those ages would not have been unlike that still existing near the coasts of the Barents and Kara Seas. Over the submerged region southward, and in some cases more or less eastward, currents would be prevalent; though changes of wind† would often affect the drift of the floating ice-rafts. But though the submergence hypothesis is obviously free from the serious difficulties which have been indicated in discussing the other one, gives a simple explanation of the presence of marine organisms, and accords with what can be proved to have occurred in Norway, Waigatz Island, Novaia Zemlya, on the Lower St. Lawrence, in Grinnell Land, and elsewhere (see "Ice Work, p. 221, and *Geol. Mag.*, 1900, p. 289), it undoubtedly involves others. One of them—the absence of shore terraces, caves, or other sea marks—is perhaps hardly so grave as it is often thought to be. It may be met by the remark that unless the Glacial Age lasted for a very long time and the movements were interrupted by well-marked pauses, we could not expect to find any such record. In regard also to another objection, the rather rare and sporadic occurrence of marine shells, the answer would be that, on the Norway coast, where the ice-worn rock has certainly been submerged, sea-shells are far from common, and occur sporadically in the raised deltaic deposits of the fjords.‡ An advocate of this view might also complain, not without justice, that, if he cited an inland terrace, it was promptly dismissed as the product of an ice-dammed lake, and his frequent instances of marine shells in stratified drifts were declared to have been transported from the sea by the lobe of an ice-sheet; even if they have been carried across the path of the Arenig ice, more than forty miles, as the crow flies, from the Irish Sea up the Valley of the Severn, or forced some 1300 feet up Moel Tryfaen.* The difficulty in the latter case, he would observe, is not met by saying the ice-sheet would be able to climb that hill "given there were a sufficient head behind it" (P. F. Kendall in Wright's "Man and the Glacial Period," p. 171). That ice can be driven uphill has long been known, but the existence of the "sufficient head" must be demonstrated, not assumed. There may be "no logical halting-place between an uplift of 10 or 20 feet to sursurface, and are sometimes found, as already stated, up to mount a *roche moutonnée* and an equally gradual elevation to the height of Moel Tryfaen," yet there is a common-sense limitation, even to a destructive *sorites*. The argument, in fact, is more specious than valid, till we are told approximately how thick the northern ice must be to produce the requisite pressure, and whether such an accumulation would be possible. The advocates of land-ice admit that, before it had covered more than a few leagues on its southward journey its thickness was less than 2000 feet, and we are not entitled, as I have endeavoured to show, to pile up ice indefinitely on either our British highlands or the adjacent sea-bed. The same reason also forbids us largely to augment the thickness of the latter by the snowfall on its surface, as happens to the Antarctic barrier ice. Even if the thickness of the ice-cap over the Dumfries and Kirkcudbright hills had been about 2500 feet, that, with every allowance for viscosity, would hardly give us a head sufficient to force a layer of ice from the level of the sea-bed to a height of nearly 1400 feet above it and at a distance of more than 100 miles.

Neither can we obtain much support from the instance in Spitzbergen, described by Professors Garwood and Gregory, where the Ivory Glacier, after crossing the bed of a valley, had transported marine shells and drift from the floor (little above sea-level) to a height of about 400 feet on the opposite slope. Here the valley was narrow, and the glacier had descended from an inland ice-reservoir, much of which was at least 2800 feet above the sea, and rose occasionally more than a thousand feet higher (*Quart. Journ. Geol. Soc.*, 1898, liv., 205; earlier observations of some upthrust of materials by a glacier are noted on p. 219).

But other difficulties are far more grave. The thickness of the chalky boulder clay alone, as has been stated, not unfrequently exceeds 100 feet, and, though often much less, may have been reduced by denudation. This is an enormous amount to have been transported and distributed by floating ice. The materials also are not much more easily accounted for by this than by the other hypothesis. A continuous supply of well-worn chalk pebbles might indeed be kept up from a gradually rising or sinking beach, but it is difficult to see how, until the land had subsided for at least 200 feet, the chalky boulder clay could be deposited in some of the East Anglian valleys or on the Leicestershire hills. That depression, however, would seriously diminish the area of exposed chalk in Lincolnshire and Yorkshire, and the double of it would almost drown that rock. Again, the East Anglian boulder clay, as we have said, frequently abounds in fragments and finer detritus from the Kimeridge and Oxford clays. But a large part of their outcrop would disappear before the former submergence was completed. Yet the materials of the boulder clay, though changing as it is traced across the country, more especially from east to west, seem to vary little in a vertical direction. The

* See for instance the courses of the Medway and the Beult over the Weald clay (C. Le Neve Foster and W. Topley, *Quart. Journ. Geol. Soc.*, 1865, xxi., 443).

† See *ante*, and for the currents now dominant consult Dr. H. Bassett in Professor Herdman's "Report on the Lancashire Sea Fisheries," *Trans Biol. Soc. Liverpool*, 1910, xxiv., 123.

‡ If, as seems probable, the temperature was changing rather rapidly the old fauna would be pauperised, and the new one make its way but slowly into the British fjords.

* Critics of the submergence hypothesis seem to find a difficulty in admitting downward and upward movements, amounting sometimes to nearly 1400 feet during Pleistocene Ages; but in the Northern part of America the upheaval, at any rate, has amounted to about 1000 feet, while on the western coast, beneath the lofty summit of Mount St. Elias, marine shells of existing species have been obtained some 5000 feet above sea-level. It is also admitted that in several places the preglacial surface of the land was much above its present level. On the Red River, whatever be the explanation, foraminifers, radiolarians, and sponge spicules have been found at 700 feet above sea-level, and near Victoria, on the Saskatchewan, even up to about 1900 feet.

instances, also, of the transportation of boulders and smaller stones to higher levels, sometimes large in amount, as in the transference of "bockram" from outcrops near the bed of the Eden valley to the level of the Stainmoor Gap, seem to be too numerous to be readily explained by the uplifting action of shore-ice in a subsiding area. Such a process is possible, but we should anticipitate it would be rather exceptional.

Submergence also readily accounts for the above named sands and gravels, but not quite so easily for their occurrence at such very different levels. On the eastern side of England gravelly sands may be found beneath the chalky boulder clay from well below sea-level to three or four hundred feet above it. Again, since, on the submergence hypothesis, the lower boulder clay about the estuaries of the Dee and the Mersey must represent a deposit from piedmont ice in a shallow sea, the mid-glacial sand (sometimes not very clearly marked in this part) ought not to be more than forty or fifty feet above the present Ordnance datum. But at Manchester it reaches over 200 feet, while near Heywood it is at least 425 feet. In other words, the sands and gravels, presumably (often certainly) mid-glacial, mantle, like the upper boulder clay, over great irregularities of the surface, and are sometimes found, as already stated, up to more than 1200 feet. Either of these deposits may have followed the sea-line upwards or downwards, but that explanation would almost compel us to suppose that the sand was deposited during the submergence and the upper clay during the emergence; so that, with the former material, the higher in position is the newer in time, and with the latter the reverse. We must not, however, forget that in the island of Rügen we find more than one example of a stratified gravelly sand between two beds of boulder clay (containing Scandinavian erratics) which present some resemblance to the boulder clays of Eastern England, while certain glacial deposits at Warnemünde, on the Baltic coast, sometimes remind us of the Contorted Drift of Norfolk.

Towards the close of the Glacial Epoch, the deposition of the boulder clay ceased* and its denudation began. On the lower plateaux of the Eastern Counties it is often succeeded by coarse gravels, largely composed of flint, more or less water-worn. These occasionally include small intercalations of boulder clay, have evidently been derived from it, and indicate movement by fairly strong currents. Similar gravels are found overlying the boulder clay in other parts of England, sometimes at greater heights above sea-level. Occasionally the two are intimately related. For instance, a pit on the broad, almost level, top of the Gogmagog Hills, about 200 feet above sea-level and four miles south of Cambridge, shows a current-bedded sand and gravel, overlain by a boulder clay, obviously rearranged; while other pits in the immediate neighbourhood expose varieties and mixtures of one or the other material. But as true boulder clay occurs in the valley below, these gravels must have been deposited, and that by rather strong currents, on a hill-top—a thing which seems impossible under anything like the existing conditions; and, even if the lowland were buried beneath ice full 200 feet in thickness, which made the hill-top into the bed of a lake, it is difficult to understand how the waters of that could be in rapid motion. Rearranged boulder clays also occur on the slopes of valleys† which may be explained, with perhaps some of the curious sections near Sudbury, by the slipping of materials from a higher position. But at Old Oswestry gravels with indications of ice action are found at the foot of the hills almost 700 feet below those of Gloppa.

Often the plateau gravels are followed at a lower level by terrace gravels,‡ which descend towards the existing rivers, and suggest that valleys have been sometimes deepened, sometimes only re-excavated. The latter gravels are obviously deposited by rivers larger and stronger than those which now wind their way seawards, but it is difficult to explain the former gravels by any fluviatile action, whether the water from a melting ice-sheet ran over the land or into a lake, held up by some temporary barrier. But the sorting action of currents in a slowly shallowing sea would be quite competent to account for them, so they afford an indirect support to the hypothesis of submergence. It is, however, generally admitted that there have been oscillations both of level and of climate since any boulder clay was deposited in the districts south of the Humber and the Ribble. The passing of the Great Ice Age was not sudden, and glaciers may have lingered in our mountain regions when palæolithic man hunted the mammoth in the valley of the Thames, or frequented the caves of Devon and Mendip. But of these times of transition before written history became possible, and of sundry interesting topics connected with the Ice Age itself—of its cause, date, and duration, whether it was persistent or interrupted by warmer episodes, and, if so, by what number, of how often it had already recurred in the history of the earth—I must, for obvious reasons, refrain from speaking, and content myself with having endeavoured to place before you the facts of which, in my opinion, we must take account in reconstructing the physical geography of Western Europe, and especially of our own country, during the Age of Ice.

Not unnaturally you will expect a decision in favour of one or the other litigant after this long summing up. But I can only say that, in regard to the British Isles, the difficulties in either hypothssis appear so great that, while I consider those in the "land-ice" hypothesis to be the more serious, I cannot as yet declare the other one to be satisfactorily established, and think we shall be wiser in working on in the hope of clearing up some of the perplexities. I may add that, for these purposes, regions like the northern coasts of Russia and Siberia appear to me more promising than those in closer proximity to the North or South Magnetic Poles. This may seem a "lame and impotent conclusion" to so long a disquisition, but there are stages in the development of a scientific idea when the best service we can do it is by attempting to separate facts from fancies, by demanding that difficulties should be frankly faced instead of being severely ignored, by insisting that the giving of a name cannot convert the imaginary into the real, and by remembering that if hypotheses yet on their trial are treated as axioms, the result will often bring disaster, like building a tower on a foundation of sand. To scrutinise, rather than to advocate any hypothesis, has been my aim throughout this address, and, if my efforts have been to some extent successful, I trust to be forgiven, though I may have trespassed on your patience and disappointed a legitimate expectation.

* Probably deposits of a distinctly glacial origin (such as those near Hessle in Yorkshire) continued in the northern districts, but on these we need not linger.

† For instance, at Stanningfield in the valley of the Lark.

‡ These contain the instruments worked by palæolithic (Acheulean) man who, in this country at any rate, is later than the chalky boulder clay.

Atomic Weight of Radium Emanation.—A. Debierne.—The method used by the author to determine the atomic weight of radium emanation was a modification of that employed by Bunsen to find gas densities, and depended upon the rate of flow of the gas through a small aperture in a thin wall. The author used a sheet of platinum for his partition, its thickness being 0·01 mm., and first experimented with gases of known molecular weight (oxygen, carbon dioxide, argon), obtaining very satisfactory results. When the method was applied to radium emanation it was found that the molecular weight is approximately 220, the difference in the various results amounting to 2 or 3 per cent. If the emanation is monatomic this number also represents the atomic weight. It agrees very well with the theory for radium of atomic weight 226·5, is transformed into the emanation with loss of an α-particle, *i.e.*, of an atom of helium of atomic weight 4. Thus the atomic weight of the emanation should be 222·5.—*Comptes Rendus*, cl., No. 26.

NOTICES OF BOOKS.

Spark Spectra of the Metals. By Charles E. Gissing, F.R.G.S., Member of the Society of Arts, Rear-Admiral R.N. (retired). London: Baillière, Tindall, and Cox.

This collection of fifty photographic spark-spectra has been prepared by the author, using a dense glass prism spectrograph by Hilger and Wratten's panchromatic plates; they are limited to the visible portion of the spectrum from λ3888 and λ7724, and an accuracy of 1 Angström unit is claimed. There is a short introduction dealing with the details of the spectrograph and the coil, the arrangement and manipulation of the secondary battery, &c. Reproductions of the spectra of forty-four elements are given, including hydrogen and helium; and six alloys, and brass, German silver, magnalium, type metal, and gold and silver coins, and a brief description is given of each experiment. The reproductions are by the half-tone process. Unfortunately no attempt has been made to eliminate the air-lines, and the spectra are therefore complicated. A scale of wave-lengths is printed at the bottom of each some distance below the lines, but it is by no means accurate, some of the divisions being twice the width of the adjacent ones; they are evidently ruled by hand. For these reasons the scale is practically useless, and although an accuracy of one unit is claimed, it would be found exceedingly difficult to determine the wave-lengths of the lines shown with any approach to that precision. On the whole, the practical utility of the atlas is very limited, but its appearance is to be welcomed as showing that the preparation of photographed spectra no longer presents any great difficulty, and that the usefulness of the spectroscope as an aid to research is becoming generally recognised.

Practical Sanitation. By George Reid, M.D., D.P.H. With an Appendix on Sanitary Law by Herbert Manley, M.A. Cantab., M.B., D.P.H. Fifteenth Edition. London: Charles Griffin and Company, Ltd. 1910.

The last edition of this work was issued so recently, and gave such a complete account of the principles and practice of sanitation, that the new edition has required very little revision. The most important additions in it relate to the ventilation and warming of school buildings. The author is a strenuous advocate of modern theories on this question, and lays special stress on the defects in the older methods of providing for ventilation in schools. Full accounts are given of the tests he has carried out in buildings of the modern Staffordshire type, and the results provide a striking argument against the old form with a central hall. In matters of detail the new edition has undergone some slight alteration, and statistics have been brought down to the latest possible date.

Oil. By C. Ainsworth Mitchell. London, Bath, and New York: Sir Isaac Pitman and Sons, Ltd.

This small book gives a popular account of the nature, origin, properties, and uses of all substances which are included under the name "oil," *i.e.*, animal, vegetable, essential, and mineral oils. The information is in all cases well chosen, only typical products being treated, and these are discussed in outline only. The illustrations of such subjects as cutting lavender, peppermint harvest, &c., are no doubt inserted for the benefit of the general reader, who will find the book sufficiently lightly written to provide pleasant reading which is at the same time instructive, while the merchant or business man will be able to gather from it, at any rate, as much as he is likely to remember about the oils, and the titles of works which he will find valuable for further reference are mentioned in the preface.

Fertilisers for Wheat Soils. By Milton Whitney. Washington: Government Printing Office. 1910.

This bulletin gives a summary of the results of the fertiliser tests on wheat soils which have been carried out at the different experiment stations attached to the United States Bureau of Agriculture. The tests, which have been continued over long periods of time, both in America, at the Ohio and Pennsylvania stations, and in England at Rothamsted, are also included, and, finally, the general conclusions to be drawn from the results obtained are discussed. It is found that the chances of increased production are greater when mixtures of two or three fertilisers are applied than when only a single substance is used, but on an average the increased value of the crop does not exceed the cost of the fertiliser. Small applications of one fertiliser appear to yield as good an increase as larger amounts, and there seems to be no evidence of a cumulative effect of long continued applications.

MISCELLANEOUS.

Solubility of Insoluble Silver Salts.—G. Stafford Whitby.—The author publishes results of the determination of the solubility of silver chloride, chromate, oxide, and other salts obtained by the direct chemical method. These results agree very well with those obtained by the conductivity method.—*Zeit. Anorg. Chemie*, 1910, lxvii., No. 1.

Brussels Exhibition.—As it has only been found possible to allot space in the Chemical Court of the reconstituted British Section of the Brussels Exhibition to little more than half of the original exhibitors, Sir Boverton Redwood, Chairman of the Chemical Industries Committee, has addressed the following letter to the remaining firms, and it is hoped that this novel suggestion will be unanimously adopted:—

"Gentlemen,—The response to the circular-letter of the Director of the Exhibitions Branch of the Board of Trade, dated August 18th, has been so prompt and generous that considerable difficulty has been experienced in allocating space to all those who have expressed their willingness to exhibit in the reduced area available for the reconstitution of the British Section, and no further applications for show cases can be considered. In view, however, of the high appreciation which the exceptionally meritorious exhibits illustrating the British Chemical Industries met with at the hands of the International Jury, I am sure that it will be the unanimous wish that there should be, during the remainder of the period for which the Exhibition will remain open, some record of those exhibits which cannot be replaced, and, as Chairman of the Chemical Industries Committee, I beg that you will furnish a descriptive account of your exhibit, with photographs if possible, which can be exhibited in a suitable frame on a wall space which has been appropriated for the purpose. It is suggested that a convenient size for such a frame would be four feet by three feet, but in exceptional circumstances it is hoped that it may be found possible to find space for a larger frame. As the new British Section is to be formally opened on September 15th, I trust that you will kindly give this matter your immediate attention and let me hear from you as soon as possible. I would add that frames of the dimensions indicated above will be supplied free of cost by the Exhibitions Branch of the Board of Trade, to whom your photographs should be forwarded at the earliest possible date.—Yours faithfully, Boverton Redwood, Chairman of the Chemical Industries Committee."

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ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

Sheffield, 1910.

By J. E. STEAD, F.R.S., F.I.C., F.C.S., President of the Section.

It was with considerable diffidence that I accepted the position of President of this section. The long list of illustrious and eminent chemists who have occupied the Chair in the past, scientists of the highest attainments, and usually professors of our educational institutions, is indicative of the very high standard to be followed. As, however, it was urged that a President with experience in the metallurgy of iron and steel was desired, I bowed to the decision of the Council, concluding that even as a mere layman I might, in this Address, discuss one or more subjects to which prominent metallurgists have for the past thirty years directed their earnest attention, both in Europe and America. I refer to some of the underlying phenomena connected with the effect of sulphur and silicon on the carbon condition of commercial cast-iron.

The effect of sulphur and silicon on cast-iron has received the attention of Karsten, Percy, Weston, Howe, Keep, West, Dillner, Bachman, Summershach, Wüst, Johnson, Stoughton, Hailstone, Longmuir, Adamson, Turner and Schuler, Levy, and many others. They all agree in concluding that sulphur tends to make iron white by retaining the carbon in the combined state, and that silicon tends in the opposite direction. Professor Howe and Dr. Wüst have endeavoured to arrive at the exact quantitative effect of sulphur and silicon in preventing or facilitating the decomposition of the carbides.

Howe recognised that the data available are insufficient on which to make any final conclusion.

Wüst found, by a series of trials, that in pigs containing 3·15 per cent carbon and about 1 per cent silicon, on an average 0·01 per cent sulphur prevented the separation of 0·02 per cent graphite, but that with 2 per cent silicon its effect was much less.

It is the general experience, that the effect of sulphur depends on the proportion, not only of silicon, but of the total carbon and manganese, and of the temperature at which the iron is cast, and the size and temperature of the mould into which the metal is run. Under some critical conditions 0·1 per cent sulphur may prevent the separation of 3 per cent graphite.

Howe's discovery—that the tendency of silicon, in increasing the decomposition of the carbides, is rapid at first, especially as the silicon rises from zero to 0·75 per cent, and then slower and slower with each further increase—is very important; so also is the generalisation of Messrs. Charpy and Grenet—that the separation of graphite on annealing iron which is initially white, containing the whole of the carbon in the combined condition, begins at a temperature which is the lower the greater the percentage of the associated silicon, and that the separation of graphite, once begun, continues at even lower temperatures than that at which it started.

The evidence advanced by Phillips, Prost, Campredon, Schulte, and others—that, on dissolving sulphurous irons in hydrochloric acid, all the sulphur is not given off as H_2S, and that a part either passes off as $S(CH_3)_2$ or remains behind with the solution as some organic product—was tentatively believed as indicative that the sulphur is chemically associated with the carbon and the iron.

Levy (*Journ. Iron and Steel Inst.*, 1908, No. 2), who has done much good work in the endeavour to determine the relations which exist between iron, carbon, and sulphur, in the alloys of these elements, states, as the result of his research, that there is no conclusive evidence of any chemical union.

In his tabulated results showing the amount of sulphur evolved presumably as $S(CH_3)_2$ on dissolving iron, carbon, and sulphur alloys, the maximum is 0·06 per cent, but the average is very much less.

Schulte, on the other hand, had found that from 1 per cent to 12 per cent of the total sulphur is evolved as an organic sulphur compound; and Bischoff found an even greater quantity.

The results are apparently conflicting, and it is evidently obvious that more research is required in this direction.

It has been shown by Arnold and McWilliam, and confirmed by others, that carbide of iron does not decompose into graphite and iron during the annealing of steel until it segregates into relatively large masses. Taking this as a basis Mr. Levy has advanced an explanatory hypothesis as to how it is that sulphide of iron prevents the decomposition of carbides in white irons. He had found that during the solidification of irons free from silicon and manganese, but rich in sulphur, "the sulphide separates at a temperature in the neighbourhood of 1130° C., together with, and as a component of, the austenite-cementite eutectic, forming a triple austenite-cementite-sulphide eutectic, the cementite component of which is interstratified with a jointed pearlite (by decomposition of austenite) sulphide one." He stated that:—"The presence of iron sulphide in the eutectic introduces intervening layers, which may partly ball up on annealing, but even then leave sulphide films between the cementite crystals; these act almost as emulsifiers, preventing the coalescence of the cementite portion, which is apparently a necessary preliminary to its decomposition into free carbon and iron. These layers and films are so persistent, even on slow cooling, as to retain their position between the cementite crystals, until the metal has cooled well below the temperature of decomposition, so that an iron which might otherwise become grey is retained, even on very protracted cooling, in the white form, by sulphur as sulphide; 0·25 per cent sulphur being sufficient for this purpose under the moderately protracted cooling conditions of the research. It is not improbable that the mechanical force exerted by sulphide, on separation and cooling, may also prevent the physical conditions necessary for carbide decomposition, which, as is well known, is accompanied by considerable expansion."

It is to be noted that Mr. Levy's argument is based on the effect of the sulphide films in the eutectic, preventing the segregation of the cementite into relatively large masses, which, as he expresses it, "is apparently a necessary preliminary to its decomposition."

His conclusions were based on the examination of hypo-eutectic alloys containing not more than 2·75 per cent carbon and free from massive plates of cementite.

Whilst admitting that his conclusions may be correct, as applied to the eutectic, some other explanation would be necessary if decomposition did not occur when a considerable quantity of massive cementite initially were to form in the alloy.

That stable massive cementite can be so obtained in iron sulphide alloys I shall presently show.

If it could be shown that sulphur in some form of combination with the iron and carbon does crystallise with the carbides, and that such mixture or solid solution is stable and not readily decomposed, it would be reasonable to conclude that the sulphur is responsible for the stability.

It has been suggested that silicon in iron decomposes the carbides according to the following chemical reaction: $3Si - 2Fe_3C = 3Fe_2Si - 2C$. The only objection to this explanation is that the silicon is not free in cast-iron, as was proved by Turner, and, moreover, as will be shown presently, it is combined with iron in solid solution before the carbide is decomposed.

Gontermann (*Anorg. Chem.*, 1908, Bd. 59) found that on adding pure silicon to molten iron, the iron and silicon combined with considerable rise in temperature, and I have noticed the same thing even when adding it to carburised iron.

The same authority, who has made a most careful study of the ternary alloys of the iron-carbon-silicon series, has shown that the eutectic freezing-point rises with the silicon from 1130° when silicon is absent to about 1150° when it reaches 10 per cent, and to 1175° when it is about 17 per cent, and that the carbon in the eutectic of the alloys containing between 0 per cent and 10 per cent silicon, falls as the silicon rises by about 0·3 per cent for each unit of silicon.

The same author proved that the pearlite reversion-point in these alloys rises with the silicon on an average of about 30° C. for each unit of silicon in the alloys containing between 0 and 6 per cent silicon. He concluded, but did not actually prove, that in the region of the curve of unvarying equilibrium two cementites crystallise; one a solid solution of the carbide and silicide of iron; and a second, a mixture of this with another ternary iron-silicon-carbon solid solution.

If the composition of the alloy lies between the curve of saturated silico-austenite and the curve of non-varying equilibrium, saturated silico-austenite primarily forms; and following this a secondary crystallisation of a binary eutectic consisting of this saturated austenite and silico-cementite.

In the year 1901 I described certain unique idiomorphic crystals which had been found in the hearth of a disused blast-furnace at Blaina. The crystals were more or less oxidised on their exterior surfaces. The analysis was as follows:—

	After deducting the oxygen, &c. Per cent.
Manganese	54·56
Iron	37·71
Carbon	3·91
Silicon	3·82
	100·00

A micro-examination proved the crystals to be quite homogeneous mixtures, or solid solutions. It was difficult to assign to them any definite chemical constitution. They may be considered as silico-carbides of manganese and iron, and, as will be shown presently, bear a close relation to similar crystals which primarily form during the freezing of iron-carbon-silicon alloys.

Having briefly referred to the work of a number of authorities, I now propose to describe my attempts to supplement our knowledge in this direction by a purely micro-chemical research.

In order to understand the remarks which follow, it is necessary to briefly describe the changes which occur when pure iron-iron carbide alloys pass from the liquid to the solid state as are indicated by the researches of Osmond, Roberts-Austen, Stansfield, and of Carpenter and Keeling.

In the iron alloys containing less than the eutectic proportion of 4·3 per cent carbon, described as hypo-eutectic alloys, austenite octahedral crystallites of the fir-tree type first fall out out of solution, and these continue to grow till the liquid is so impoverished of iron and enriched in carbon that when the eutectic proportion of 4·3 per cent carbon is reached, the liquid solidifies, and breaks up into carbide of iron and austenite.

The hypereutectic alloys, containing more than the eutectic proportion of carbon, on cooling, first yield carbide of iron crystals, and these continue to grow till, by removal of the excess carbon, the eutectic proportions of iron and carbon are reached. The eutectic in its turn then freezes.

For the purpose of my research it was necessary to select pig metals, grey and high in silicon and white with high sulphur. These were kindly supplied by Messrs. Wilson, Pease, and Co., and Messrs. Cochrane and Co., Middlesbrough. They were made from Cleveland ironstone, and contained:—

	White.	Grey glazed iron. No. 1.	Grey glazed iron. No. 2.
	Per cent.	Per cent.	Per cent.
Combined carbon	2·98	Nil	Trace
Graphite	Traces	2·65	3·300
Manganese	0·29	0·72	0·676
Silicon	1·89	5·21	4·321
Sulphur	0·27	0·03	0·025
Phosphorus	1·62	1·56	1·660

It may be accepted that the sulphur in the white iron undoubtedly is the cause of the whiteness of the iron, whilst the excessively high silicon and low sulphur are equally responsible for the graphitic condition of the carbon in the grey irons.

The micro-structure of the high silicon metal was characteristic of all phosphoretic, high silicon, carbon alloys. Curved plates of graphite cut the mass in many directions, whilst the binary eutectic of phosphorus and iron remained in irregular patches, generally midway between the graphite plates. The ground mass occupying the space between the eutectic and graphite plates consisted of silico-ferrite.

The interesting feature about the structure of the white iron is that there was no iron-iron-carbide eutectic. This had been replaced by the ternary eutectic of iron-phosphorus and carbon, which, according to Dr. Wüst, contains about:—

	Per cent.
Iron	91
Phosphorus	7
Carbon	2
	100

There was evidence that the primary crystals of austenite of the octahedral skeleton type had been the first to fall out of solution, that the second crystal to form consisted of short plates of carbide of iron (cementite); whilst the ternary eutectic of phosphorus, carbon, and iron was the last to freeze and occupied spaces between the cementite plates and the primary crystals.

Dr. Carpenter and his assistant, Mr. Edwards, of Victoria University, Manchester, kindly obtained, for the purpose of this Address, the cooling curves of these two typical metals. These were as follows:—

Grey Iron.

The long arrest at 1118° indicates a change of state, but is also coincident with important chemical changes. The second long arrest at 945° is due to freezing of the iron phosphorus carbon eutectic. The arrest at 850° indicates the formation of pearlite, and corresponds closely with the arrest in a similar alloy examined by Gontermann. The arrest at 690° is probably due to the formation of pearlite in the eutectic of iron and phosphorus, and is of great interest, for it points to the conclusion that silicon is not a constituent of the austenite of the ternary eutectic.

White Iron.

The micro-structure and analysis help more fully to explain the arrests on cooling this alloy.

The first arrest at 1149° C. is where the primary austenite crystallises with the silicon, as will be shown presently.

The second arrest is where the primary cementite plates freeze.

The third arrest at 945° is the freezing-point of the ternary eutectic, and is identical with that of the corresponding long arrest of the grey iron.

The fourth arrest at 770° is coincident with the formation of pearlite.

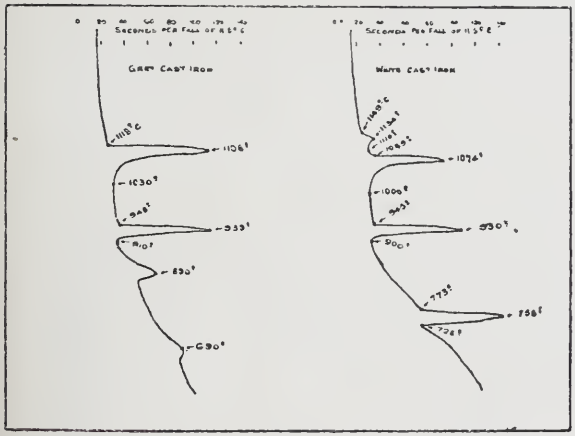
Bearing in mind that the manganese in the white iron was insufficient to combine with the whole of the sulphur present to form manganese sulphide, it is obvious that

some other compound or compounds of sulphur existed. The microscope clearly revealed the presence of manganese sulphide and traces of free iron sulphide.

The carbide plates were quite free from striations of sulphide, such as had been noticed by Mr. Levy in the eutectic of high sulphur irons.

But for the sulphur present, the silicon would have been sufficient to effect a decomposition of the carbides, and the metal in absence of the sulphur would have given a grey instead of a white fracture. In view of this conclusion it appeared to be probable that if manganese were to be melted with the metal, it would combine with the sulphur associated with iron, &c., and crystallise as MnS, previous to the solidification of the carbide, or independently, and that the metal would then become grey on cooling.

In order to test this, a portion of the metal was melted in a clay pot with a little pure manganese, free from carbon —sufficient to give 1 per cent of manganese, which was more than sufficient to combine with the whole of the sulphur. As soon as the mass was melted it was at once poured into a sand mould and allowed to set. When cold, it broke with a grey fracture corresponding to what is known as hard forge, and the combined carbon instead of being about 3 per cent was reduced to 0·6 per cent, a result proving the correctness of the hypothesis.



It is well known that when manganese or chromium and some other metals are present in large quantities in pig irons, these metals, as carbides, crystallise with the carbide of iron forming double carbides, and these are much more stable than the massive pure iron carbide. It appeared reasonable to believe that if sulphide of iron, or some iron-sulpho-carbon compound, were to crystallise with the carbides it would have a similar effect.

Remembering that the conclusions on this question, as to whether sulphur does or does not crystallise with the carbides, are conflicting, it is evident that the only possible way to find out whether sulphur does so crystallise is to separate the carbide from the iron and test it for sulphur. With this object, a considerable quantity of the original Cleveland white metal was crushed to the very finest powder. It was then treated with a 10 per cent solution of hydrochloric acid in water in large excess, and the action of the acid was allowed to continue until evolution of gas ceased. The insoluble matters, consisting mainly of carbides and phosphides, were filtered off, washed and dried, and were ground down in an agate mortar to a still finer powder, so as to liberate any mechanically entangled sulphides. The powder so dealt with was again treated with acid as before, after which the residue was filtered off, thoroughly washed with water, was transferred to a separate vessel, and was boiled with strong caustic-potash to dissolve any decomposition products.

The residue was again filtered off, was washed and dried, and submitted to analysis. The residue when dried weighed about 45 per cent of the original metal, and contained as follows :—

	Per cent.	
Iron	92·43	
Carbon . ..	6·06	
Silicon.. ..	0·12	
Sulphur ..	0·12	
Phosphorus .	0·97	(6·2 per cent phosphide of iron)
Water, &c...	0·30	
	100·00	

A second trial was made with the same metal; but, in this case, re-pounding and acid treatment were repeated three times, so as to eliminate the possibility of mechanical inclusion of sulphide or iron. The sulphur found in the remaining carbides was 0·1 per cent.

As the manganese in this metal was not sufficient to form manganese sulphide with the sulphur, it seemed desirable to determine whether or not when the manganese is in sufficient quantity sulphur would crystallise with the carbide. For this purpose the white chilled part of a crushing roll was experimented upon. The centre part was open grey iron, and contained 3·1 per cent of the carbon as graphite.

The white chilled portion contained :—

	Per cent.
Combined carbon	3·75
Graphitic carbon	Trace
Manganese	0·65
Silicon	0·70
Sulphur	0·10
Phosphorus	0·23

It was crushed to powder and treated exactly in the same way as previously described for the separation of carbide. The residue contained by analysis :—

	Per cent.
Silicon	0·028
Sulphur	0·016

a result showing that only a minute quantity of sulphur was crystallised with the carbide. Whether a different result would follow if both sulphur and manganese were greatly increased has yet to be determined.

Having proved that sulphur in some undetermined state of chemical combination does crystallise with carbide of iron, an attempt was made to determine the maximum amount of that element the carbide will retain under the most favourable conditions. With this object in view a considerable quantity of very pure white iron, containing only traces of silicon, sulphur, and phosphorus, and 3·5 per cent of carbon, was melted in a plumbago crucible; and when in a molten condition sticks of roll sulphur were forced under the surface of the metal, and afterwards the mixture was briskly shaken up with the sulphur which had liquefied on the surface.

Precisely the same result was obtained as described by Karsten, who had made a similar experiment. A metal was produced having a white fracture and large cleavage faces. The micro-structure was similar to that of hyper-eutectic iron carbon alloys. Large plates of carbide cut the metal in many directions, whilst between the carbide plates was located the triple carbide-sulphide-pearlite eutectic, so accurately described by Mr. Donald Levy.

The carbide plates themselves were peculiar in having circular prismatic inclusions of sulphide of iron symmetrically arranged at right angles to the sides of the plates. In horizontal sections of these plates they appeared as circular dots, sometimes arranged in continuous lines, suggesting that the sulphide had been actually in solution with the carbide when the metal was liquid, that they fell out of solution together, the sulphide separating and segregating along the cleavages of the carbide.

A portion of this sulphurous material was re-melted and treated with a second quantity of sulphur. This time in addition to sulphide of iron a considerable quantity of the soot-like substance described by Karsten floated to the surface, and free graphite separated and stuck to the sides of the crucible.

The analyses of these metals are as follows:—

	After the first addition of sulphur. Per cent.	After the second treatment with sulphur. Per cent.
Carbon ..	4·37	4·39
Sulphur ..	1·00 (about)	1·00
Silicon ..	0·03	0·05

From which we may conclude that the maximum degree to which the carbon can be concentrated by this method is about 4·4 per cent. In these trials the carbide certainly had sufficient opportunity to become saturated with sulphur in each case. Both of the metals were crushed to exceedingly fine powder, and were treated with acid to decompose the free sulphides. The residues were repounded and treated with acid a second time, and afterwards with strong potash solution. After this treatment, analyses of the insoluble residues indicated, in one case 0·09 per cent sulphur, and in the other 0·08 per cent. *From this it would appear that carbides will not carry in solid solution more than about 0·1 per cent of sulphur.*

The metal containing 4·37 per cent carbon and 1 per cent sulphur, even on prolonged annealing, did not become graphite, a proof that the massive carbides present were quite stable.

The microscope reveals the fact that in almost all commercial white irons containing much sulphur the greater part of the sulphur is combined with either manganese or iron, and that the sulphides mainly exist as independent inclusions. It appears reasonable to assume that the manganese sulphide is without influence on the carbon condition, and that, although iron sulphide may have some influence, in the way suggested by Mr. Levy on the eutectic, *it is the sulphur that crystallises with the carbide which is mainly responsible in preventing the separation of graphite by making the carbide more stable.*

If it is assumed that the stability of the carbide depends on the quantity of sulphur which crystallises with it, and not on the total amount present in the metal carrying the carbides, it is clear that a great field of research is now open, the borders of which I have barely touched to correlate their stability and sulphur contents.

The microscope does not show in what constituent the silicon crystallises. It is known that in grey irons it is associated with the ferrite and pearlite, but grey iron is the final result of the decomposition of carbide of iron and possibly of silico-carbides, which primarily form during solidification, and although the silicon in the decomposed product may be entirely associated with the iron it is no proof that initially some of it may not have crystallised with the carbides.

In the white Cleveland iron, previously referred to, it is probable that the several constituents are present in the following proportions:—

	Per cent.
Silico-pearlite, the residue of the original austenite octahedral crystallites	42·50
Iron carbide in plates	33·66
Iron, phospho-carbide eutectic	23·10
Manganese sulphide	0·38
Iron sulphide	0·36
	100·00

When fractionally dissolving the powdered metal in acid, it was the iron and associated silicon of the pearlite which passed into solution, and the carbide and phosphide hich remained insoluble, and as these contained only per cent silicon, or about 0·6 per cent on 100 parts of original metal, it is evident that the pearlite must have contained $1·89 - 0·06 = 1·83$ per cent of the silicon, or on 100 parts of it $\frac{100 \times 1·83}{42·5} = 4·3$ per cent, and that about 97 per cent of the total silicon had crystallised with the austenite.

A little reflection will lead to the conclusion that if the carbon in the Cleveland white iron were to be gradually increased, the proportion of primary austenite crystallites would decrease, there would be less and less of them to carry the silicon, and this element would be concentrated in the diminishing solid austenite. It also follows, that if the carbon were to be so increased that no primary austenite would form, the silicon would have to crystallise in some other constituent.

In the example, referred to above, of the chilled casting, the carbides contained only 0·028 per cent silicon, or 0·016 per cent on the original metal. In this case, therefore, about 98 per cent had crystallised with the primary austenite.

The question as to what amount of silicon will crystallise with the austenite so as to saturate it is probably variable with other variables. To determine this by chemical analysis would involve an exceedingly tedious research.

It is probable that as it increases, and as the austenite approaches more and more nearly to the saturation point, a gradually increasing proportion of the silicon will crystallise with the carbides.

It is well known that molten low silicon grey irons, in the absence of any appreciable quantity of sulphur, gives a white fracture when slightly chilled. Irons with above 5 per cent silicon, when similarly treated, are supposed not to behave in the same manner; and this is quite true when any ordinary method of chilling is adopted. For instance, when the liquid silicious glazed metal No. 1 was run into water, the chilled iron contained graphite; but when a large drop was suddenly pressed into a sheet as thin as paper between cold plates of iron, the chilled metal was quite white and no graphite could be detected on dissolving it in nitric acid. The metal so chilled was difficult to dissolve in acid, and the silica produced, instead of forming a gelatinous bulky residue. remained in a close dense condition—indeed the thin chilled sheet, after all soluble matter had been removed, remained a rigid sheet of dense coherent silica, whereas the same metal allowed to cool slowly from the liquid state in a sand mould yielded to acid gelatinous silica.

The different behaviour to acid treatment of the chilled as contrasted with that of the slowly-cooled metal indicates that the condition of the silicon in rapidly chilled metal is different from its condition in the same metal slowly cooled.

In 1895 Mr. T. W. Hogg, of Newburn Steel Works, published an account of a very interesting observation, in which he showed the difference in the silicon solubility in different parts of the same pig-iron—a portion of which was white and a portion grey. The iron referred to contained:—

	White part. Per cent.		Grey part. Per cent.	
Combined carbon..	3·88	4·33	0·98	4·66
Graphitic carbon ..	0·45		3·68	
Silicon	0·65		0·85	
Manganese	1·63		1·60	

He determined the solubility in dilute acid of the silicon in each portion, and found that the silicon soluble in hydrochloric acid was, in the grey part = about 81 per cent and in the white part = about 48 per cent.

He found also that the silica left on treating the two varieties of metal in acid differed in character—that from the white portion was dense, whilst that from the grey metal was much more voluminous. The white metal contained the eutectic proportion of carbon, and therefore it could not contain any austenite crystallites; indeed with the silicon 0·60 per cent also present it must be regarded

as a hypereutectic alloy, and on that account we are forced to conclude that the silicon must have crystallised with the carbide.

It has long been known that on dissolving grey ferro-silicon containing even 6 per cent silicon the silica gelatinises, whereas when the silicon approaches 10 per cent much of the silica remains in a dense form. It is almost certain that during the solidification of the grey part of Mr. Hogg's pig-iron a rich silicon cementite must have primarily formed, for the high carbon would not allow the formation of any primary silico-austenite; when this cementite decomposed the silicide part of it would become diluted with the iron of the decomposed carbide. It was, no doubt, this diluted solid solution in the cold grey metal which yielded the gelatinous silica.

That silicon does diffuse into iron, even at relatively low temperature, was proved by Lebeau. He found that free silicon and iron, when heated together *in vacuo* at 960° C., chemically combine, a fact I have fully confirmed, although it is impossible to get silicon to combine with iron on heating them together in a cementation furnace where oxidising gases have access to the silicon.

To determine whether silicide of iron would diffuse into and precipitate the graphite in white iron, a sample of crushed white iron free from impurities, containing 3·5 per cent of carbon, was mixed with 10 per cent by weight of a silicon alloy containing 20 per cent of silicon ($=Fe_2Si$) also in powder. The mixture after compression in a short piece of iron tube was heated for two hours at 1000° C., in an atmosphere of hydrogen gas, and was then removed and cooled in air.

For comparison a portion of the crushed white iron was treated in the same way.

The combined carbon in the metals before and after heating were as follows :—

	Before. Per cent.	After. Per cent.
In white metal alone	3·5	3·44
In white metal and silicide ..	3·20	0·60

Not only does this trial prove that silicide does diffuse into carbide of iron and precipitate graphite, it has also an important bearing on the question as to why silicon in pig-iron, even in small quantities, causes the carbide to be decomposed. In the experiments with the chilled part of a casting containing only 0·7 per cent silicon and 3·75 per cent carbon it was shown that the carbide contained only 0·028 per cent silicon, and that 98 per cent of the total silicon was concentrated in the pearlite; yet this white iron on heating to 1000° C. became quite grey. *Are we not justified in concluding that it was the diffusion of silicide of iron from the silico-austenite into the carbides which caused the separation of graphite?*

As I had proved, first that sulphur crystallises with and makes the carbide of iron more stable, and second that in the presence of a fusible mother-liquor rich in phosphorus, after the austenite crystallisation is complete, the carbide crystallises out in plates and not as iron carbide eutectic, it appeared probable that if, as Gontermann premised, two kinds of cementite actually form during the solidification of iron-carbide-silicon alloys, it might be possible to obtain them in a separate state by melting the rich silicon alloys with a little sulphur.

In order to test this a portion of the No. 1 grey glazed metal was melted, and when fluid a little sulphide of iron was mixed with it. The mixture was then cast in sand. Owing to the rapidity of the melting some of the graphite escaped and floated on the surface of the metal.

When cold it was found that the lower part of the small casting gave a white fractured surface, whilst the upper part was close grey.

The analyses are given in the accompanying table (see next column).

	White part. Per cent.	Grey part. Per cent.
Combined carbon ..	2·06	0·60
Graphite	Trace	1·46
Manganese	0·03	0·03
Silicon	5·41	5·40
Sulphur	0·88	0·91
Phosphorus	1·50	1·50

The grey part, although slowly attacked by cold acid, did dissolve, yielding much voluminous silica. The white part was almost inert and only dissolved in strong hydrochloric acid with difficulty, and when the iron was dissolved out the remaining silica was of the dense variety, from which it would appear that the effect of the sulphide is akin to that of sudden quenching.

It was the micro-structure of the white portion, however, which was of unique interest. On "heat-tinting" two kinds of hard crystals appeared, one more readily coloured by heating than the other. The more resistant crystals were idiomorphic, and were furnished with their terminal angles, but as they were embedded in the surrounding metal it was impossible to form any exact idea of the crystalline system to which they belonged.

The second order of crystals had evidently solidified at a later period, as their forms were interfered with by those of the idiomorphic type; they were much like ordinary plates of carbide of iron. The ground mass contained indications of octahedral on fir-tree crystallites and a well-developed phosphorus iron eutectic of the honeycomb type. This eutectic was the last to freeze, as it filled the spaces between the plates of the hard crystals. There was no pearlite excepting in the eutectic of phosphorus and iron. We can only tentatively conclude that of the two cementites the idiomorphic crystals contained the greater part of the silicon because of their greater resistance to oxidation, and probably consisted of carbo-silicide of iron, with sufficient sulphur in them to make them stable; also that the second crystals were carbide of iron, possibly containing a lesser quantity or no silicide in solid solution.

A further series of experiments was made on a portion of the same metal. In this case the molten iron was mixed and agitated with free sulphur instead of sulphide of iron, and the metal was at once poured into a sand mould in a thin layer. When cold it was quite white in fracture and had large brilliant cleavage faces.

It had the following composition :—

	Per cent.
Combined carbon	2·60
Manganese	Trace
Silicon	6·65
Sulphur	0·93
Phosphorus	2·08

The sulphur had evidently effected concentration of the silicon phosphorus and carbon by removing some of the iron, as sulphide of iron was actually formed and floated on the surface of the iron. It was fractionally dissolved as described in previous cases, and the residue (72 per cent of the weight of the original metal) was tested and found to contain :—

	Per cent.
Carbon	2·92
Manganese	Trace
Silicon	6·70
Sulphur	0·062
Phosphorus	1·410

This insoluble fraction evidently consisted of both classes of crystals, together with some phosphide of iron. Efforts were made to separate the crystals by chemical means, but without success.

On the long and continued action of strong hydrochloric acid a residue was obtained containing a little less carbon and more silicon than were present in the mixture, a

indication that the less soluble portion is different from that more soluble.

The micro-structure was similar to that of the metals of the previous trial, but as the carbon and silicon were higher the carbo-silicide was in greater quantity. It crystallised in long flat plates and not in relatively short idiomorphic crystals.

It is probable exception may be taken, with some justification, that the sulphur does not simply arrest the decomposition of the cementites, which I have premised primarily form, but may act in some other unknown way. An attempt was therefore made to find out whether they could be obtained by some other method without the aid of sulphur. As it is known that the ternary eutectic of iron, phosphorus, and carbon melts at about 945° C., it appeared probable that if silicon in small quantity were to be melted with an iron-carbon phosphorus alloy very rich in phosphorus the two kinds of cementites would fall out of solution at a lower temperature, and would probably not decompose into graphite and silico-austenite in cooling down after their formation. To ascertain whether or not this would be the case, a fusible iron-phosphorus-carbon alloy containing more than the eutectic proportion of carbon was made. It had the following composition :—

	Per cent.
Iron	91·89
Phosphorus	5·37
Carbon	2·62
Silicon, &c.	0·10
Sulphur	0·02
	100 00

Four hundred grms. were melted with sufficient silicon alloy to yield in the mixture :—

	Per cent.
Carbon	2·4
Phosphorus	5·0
Silicon	2·90
Sulphur	0·02

When melted a portion of it was cast in a sand mould, the remainder was allowed to cool in the crucible.

When cold, that cooled in the crucible was quite grey, whilst the portion cooled in sand was white at the lower part and grey on the top part of the casting, results which proved that the alloy was very unstable and that decomposition of the lower part of the casting was arrested by the slight chilling effect of the cold sand.

On microscopic examination of the white portion the ground mass was found to consist of the binary phosphorus iron eutectic, whilst two different cementities were embedded in it, one much more rapidly coloured on "heat-tinting" than the other. The colours of the constituents of the properly heated and polished metal were as follows :—

Cementite (*a*)	White
,, (*b*)	Red
Phosphide of iron	Purple
Iron pearlite crystallites	Grey

The part which broke with a grey fracture consisted of octahedral crystallites of silico-pearlite, the binary phosphorus iron eutectic, and undecomposed (red) cementite crystals, but there was a complete absence of the (white) cementite crystals. Graphite was also present in exceedingly fine plates, resembling what is known as temper graphite.

The evidence here is conclusive that even in the absence of sulphur :—

1st. Two cementites had formed.

2nd. That one cementite is much more unstable than the other variety, and decomposes in advance into silico-austenite and graphite,

Having proved that two different kinds of cementite do actually form and crystallise in the phosphorus eutectic, it remained to ascertain in what way these crystallise in the absence of the phosphorus eutectic.

For this purpose two hypo-eutectic alloys were prepared without any phosphorus, but with sufficient sulphide of iron to check the decomposition of the carbides. They contained :—

	1. Per cent.	2. Per cent.
Carbon	2·40	2·10
Silicon	3·17	7·10
Sulphur	1·21	0·82
Phosphorus	0·02	0·02

These when cold after casting in sand broke with white fractures.

The carbides separated in the manner previously described contained :—

	1 Per cent.	2. Per cent.
Carbon	6·16	3·00
Sulphur	0·09	0·08
Silicon	0·97	7·93
Percentage of carbides insoluble in acid	27·5	50·00

The repeated acid treatment in this, as in all previous cases, no doubt dissolved a portion of the carbides, and what was actually weighed represented only a part of those actually present in the alloys.

In No. 2 alloy, after polishing and "heat-tinting," the microscope proved the presence of a few fir-tree crystallites embedded in a ground mass of cementite, and a eutectic containing the two kinds of cementite, the No. 1 specimen containing a much smaller proportion of the cementite rich in silicon than No. 2.

As the metals had been somewhat rapidly cooled the alloy No. 2 was re-melted, and was then allowed to cool in the crucible, so as to obtain a more coarsely crystallised eutectic. When cold, on polishing and "heat-tinting," the eutectic was clearly seen. There were the remains of large primary silico-austenite crystallites, plates of the red-coloured cementite, and a well-developed eutectic consisting of the (red) coloured and (white) cementites.

The cooling having been slow, this compound constituent had suffered partial decomposition in isolated patches into graphite and silico-ferrite, whilst the cementite coloured red remained intact.

There can be little doubt that the residue left insoluble in acid consisted of the two cementites, but in what proportion it is impossible to tell, as a method for isolating them has yet to be found.

Had the alloy contained a greater proportion of carbon the amount of cementite rich in silicon would have been in much greater proportion.

The trials, incomplete and necessarily imperfect as they are, go far to prove, just as Gontermann premised, that during the solidification of high silicon pig-irons two cementites fall out of solution together as a eutectic mixture.

They also have proved that the carbo-silicides are exceedingly unstable, breaking up into silico-austenite almost as soon as formed. *It is the instability of these silico-carbides which is mainly responsible for the graphitic character of grey irons rich in silicon and low in sulphur.*

Summary and Conclusions.

1. The experimental results advanced show proof that carbide of iron in presence of iron sulphide crystallises with a minute quantity of sulphur not exceeding about one-thousandth's part of the weight of the carbide, but the nature of the iron-carbon-sulphur compound has not yet been determined.

2. It seems almost, if not absolutely, certain that it is the sulphur crystallised with the carbide which makes the latter stable.

3. The evidence appears to support the view, long held by some and more recently accepted by others, that during the freezing of iron-carbon-hypo-eutectic alloys after the crystallisation of the primary austenite, and in the eutectic and hypereutectic alloys, it is the carbide and not graphite which primarily forms, and that the carbide afterwards decomposes into graphite and austenite.

4. It has been proved by chemical methods that when the hypo-eutectic alloys, low in silicon, freeze, nearly all the silicon crystallises out with the primary austenite ; and it follows that on gradually increasing the carbon so as to reduce the quantity of primary austenite, the silicon remaining constant, the austenite which does form must be as gradually enriched in silicon up to saturation-point ; and, when that point is reached, the excess silicon crystallises out with a portion of the carbide of iron to form carbo-silicide of iron. Other elements remaining constant, the same result must follow on gradually increasing the silicon.

5. In the alloys of eutectic proportion and in the hypereutectic alloys, as no primary austenite can form, the silicon crystallises primarily with the carbide.

6. In Cleveland pig-iron containing about 1·5 per cent phosphorus, a ternary eutectic of iron-carbon-phosphorus takes the place of the iron-iron-carbide eutectic. In white irons containing 3 per cent carbon and under 2 per cent silicon, after the primary austenite has fallen out of solution carrying practically all the silicon, it is not iron-iron-carbide which forms, but independent plates of cementite, or carbide of iron, and after these have crystallised and the residual mother-liquor has arrived at the composition of the ternary iron-carbon-phosphorus eutectic, the latter solidifies at 945° C.

7. In Cleveland irons which become grey on cooling, and in which there is no primary austenite, the same iron-carbon-phosphorus eutectic is the only eutectic to form during cooling, and, instead of a ternary iron-carbon-silicon eutectic, two independent cementites crystallise—one a silico-carbide, and the other carbide of iron possibly containing a little silicide in solid solution. The micro-examination of the cold alloys, to which a little sulphur had previously been added when the metals were melted, led to the conclusion that it is the carbo-silico-cementite which primarily crystallises.

8. There is evidence that the primary carbo-silicides are exceedingly unstable, and are the first to decompose into graphite and silico-austenite.

9. In the absence of any sensible quantity of phosphorus, two cementites form—one the silico-carbide cementite, the other the carbide cementite—and these crystallise together as a eutectic mixture.

10. The exact composition of the two cementites has not yet been determined, as no chemical method has been found for their isolation.

11. It is evident that it is the exceedingly unstable character of the silico-carbides which is responsible for the greyness of commercial metals rich in silicon and low in sulphur.

12. Silicide of iron when heated at 1000° C. with pure white iron free from silicon effects the decomposition of the carbide of the white iron. Based on this observation the hypothesis seems justifiable, in cases where all the silicon present in hypo-eutectic alloys crystallises out with the primary austenite, that after the carbide has solidified diffusion of the silicide follows, and this leads to the decomposition of the carbide of iron into graphite of iron.

13. Many of the results arrived at by chemical analysis support the hypothetical conclusions of Gontermann, who depended mainly on the data obtained by thermal methods of treatment.

In conclusion, it will be clear from what I have stated that there are many gaps yet to be filled. I hope that the knowledge of this fact will lead others to follow up the research, which, in its present stage is far from complete.

(The Address was illustrated by several photo-micrographs).

INFLUENCE OF CHEMICAL COMPOSITION AND THERMAL TREATMENT ON PROPERTIES OF STEEL.*

By Prof. A. McWILLIAM, A.R.S.M., M.Met.

Sheffield is pre-eminently the home of the manufacture of special steels, and she attains her ends by strict attention to ultimate chemical composition, by insuring the presence of the most desirable amounts of beneficial substances, and the practicable minimum of deleterious contents, be they the well-understood, such as sulphur and phosphorus, or the more or less mysterious, such as oxygen ; and also to those thermal changes called heat treatment, that are produced, sometimes slowly, as in annealing, sometimes suddenly, as in quenching, and that vary the chemical composition or the physical nature of the several constituents, and the mechanical and other properties of their aggregate, the finished steel. Carbon is the chief of the elements that are varied to obtain the different properties required in steels, and typical examples are given of the change in properties produced by the gradual increase in the content of carbon, which, at least in normal steels, is present as carbide of iron (Fe_3C). Other elements are added to vary the properties of the steel, probably mainly by their influence on the nature, the composition, or the distribution of the carbide in the steel. The properties of a series of steels with varying carbon contents, but containing in addition about 1 per cent manganese, are shown, and a similar series containing 2 per cent chromium, all from results quite recently obtained by the author and Mr. E. J. Barnes. Examples of steels of similar carbon contents containing (1) no special element, (2) 1 per cent manganese, (3) 2 per cent chromium, (4) vanadium and chromium, (5) nickel and chromium, are tabulated to show the comparative influence of these various additions.

The effects of such heat treatments as long annealing and quenching, followed by tempering at different temperatures, on selected examples of the above special steels are explained, and finally comparative tables with carbon contents and heat treatments as nearly alike as could be selected, and varying only in the special element added, to show the very considerable and abiding influence of the fundamental chemical composition. Photo-micrographs of the more interesting types were also exhibited and described.

FERRO-SILICON ; WITH SPECIAL REFERENCE TO POSSIBLE DANGER ARISING FROM ITS TRANSPORT AND STORAGE.*

By Dr. S. M. COPEMAN, F.R.S.

The possibility of danger to life from the transport of ferro-silicon (an alloy or eutectic mixture of iron and silicon employed in the manufacture of steel) has already received official attention in this country through a "Notice to Ship-owners, Shipmasters, and Shippers" issued by the Board of Trade in September, 1907, but the magnitude of the risks involved in the treatment of this material and the need for more stringent regulations were strikingly demonstrated by the death of five Russian immigrants on board the s.s. *Ashton* in December, 1908, during this ship's voyage from Antwerp to Grimsby. Inquiries made on behalf of the Local Government Board into this occurrence brought to light a number of previous accidents in connection with the transport of ferro-silicon, and after conference with the Home Office and the Board of Trade the full investigation of the subject was entrusted to Dr. Copeman, with whom subsequently Mr. S. R. Bennett, one of H.M. Inspectors of Factories, and Dr. Wilson Hake, Lecturer on Chemistry at Westminster Hospital, collaborated.

* A Paper read before the British Association (Section B), Sheffield Meeting, 1910.

Among the accidents known to have occurred from the handling or transport of ferro-silicon may be mentioned the explosion of consignments enclosed in iron drums, the ferro-silicon in which contained about 54 or 55 per cent of silicon. But more important and much more frequent than these are the well-authenticated cases of sudden illness and death caused by the gases evolved from certain cargoes of ferro-silicon, full details of which were set out in an official report recently presented to both Houses of Parliament.

Low-grade ferro-silicon—*i.e.*, an alloy containing not more than 15 per cent of silicon—is made in blast-furnaces to a considerable extent in this country; but the high-grade variety, containing from 25 to 95 per cent of silicon can only be produced at the high temperatures attainable in the electric furnace. The latter variety is imported from certain districts in France, and, to a less extent, from Austria, Scandinavia, &c., where ample electrical energy is derivable at a low cost from water-power. About 4000 tons of this material are said to be imported annually into England, and, as serious inconvenience to steel manufacturers is being caused by the refusal of shipping firms to carry it, there is great need for regulations permitting its transport under defined conditions which will obviate accident.

The electrically produced or high-grade ferro-silicon has in recent years displaced in large measure the blast-furnace variety in the manufacture of the better qualities of steel, and as an outcome of this change the dangers of noxious fumes from the high-grade variety have gradually been realised. Manufacturers and chemists, in the light of their special experience, have come to the conclusion that it is solely or chiefly the 50 per cent variety of the high-grade material which is thus dangerous. But that the matter is in reality considerably more complicated is indicated by the results of Dr. Hake's chemical researches. It should, however, be added that some of the firms concerned have recognised the importance of porosity and liability to disintegrate as factors in the ready evolution of poisonous fumes, and the French Commission drew attention, in their report, to the safety of compact alloys. It is evident, however, that at present, unless and until sharp lines can be drawn between the different amounts of gas evolved from different samples of ferro-silicon under similar circumstances, it is impracticable with certainty to distinguish, among any of the higher percentage varieties of ferro-silicon, between safety and danger. Nevertheless, the recommendations suggested by the writer, and now officially adopted by the Board of Trade, will probably prevent the occurrence of future accidents in the transport of ferro-silicon. They comprise the need for ascertaining that the ferro-silicon has been broken into pieces of the size in which it is usually sold some time before being taken on board ship; the marking in bold letters of the certified percentage grade of each consignment on the barrel or other receptacle, and the date of manufacture; the prohibition of conveyance of ferro-silicon on passenger vessels, and the adoption of certain precautions during transport in cargo boats.

THE CRYSTALLINE STRUCTURE OF IRON AT HIGH TEMPERATURES.*

By WALTER ROSENHAIN, B.A., D.Sc.

The immediate object of the experiments was to study the mode of deformation of iron and steel under stresses applied to the metal at high temperatures. The principal questions to be decided were, whether at high temperatures the mode of deformation was still of a strictly crystalline character, such as that which has been observed at ordinary temperatures, and whether the allotropic transformations of iron affect its behaviour under strain. The method of Ewing and Rosenhain for observing the effects of strain on metals consists in preparing a properly polished surface on a specimen of suitable shape, and subsequently exposing the specimen to plastic deformation, the changes in the microscopic features of the surface being studied during, and more especially after, the application of the strain. In order to apply this method to hot metal it was necessary to devise means for heating the specimens in such a manner that even at temperatures well above 1000° C. the original polished surface would remain free from oxidation. The method adopted was that of heating the specimen electrically in a very high vacuum, and in this way specimens could be heated up to 1100° C. without injury to the surfaces. For the purpose of applying the desired strain to the specimen while heated *in vacuo*, an apparatus was devised whereby a compressed spring could be released at any desired moment by electrically fusing a wire which had kept the spring compressed; by means of a suitably arranged lever the release of this spring was caused to strain the specimen to any desired extent, while the operation could take place when the specimen had attained any desired temperature. The actual temperature of the specimen was determined by attaching to the rear or unpolished side minute particles of various salts of known fusion-points, and observing which of them had melted. The specimens used in this apparatus were thin short strips of sheet metal, and as these were heated by a direct electric current passing through them, the ends of the specimen remained a good deal colder than the middle, owing to the conduction of heat from these ends into the comparatively massive frame of the apparatus. In this way strain was applied to a strip of metal varying continuously in temperature from the middle towards each end.

The material used for the earlier experiments was a pure variety of very mild steel such as that employed for transformer-sheets, but this had been annealed in hydrogen in order to remove all traces of oxide. Subsequently other materials—all of them approximating in composition to pure iron—were employed, notably some specially prepared electrolytic iron of a very high degree of purity. The photo-micrographs accompanying the paper show that the behaviour of these different materials was closely similar.

Before describing the effects of strain, the effects of simple heating *in vacuo* must be considered, since this alone produces changes in the surface appearance. Those portions heated up to the Ac_2 point (770° C. in one of the materials used) show no changes; those portions which had attained a temperature between Ac_2 and Ac_1 (941° C. in one of the materials) show a double system of boundaries due to the volume-change which iron undergoes on passing through the change from the α to the β state. Those parts of the specimen which had been heated above Ac_1 showed, particularly in cases where the vacuum bed had not been as high as possible, a slight amount of tinting due to oxidation, and this revealed a third structure superposed on the β structure just mentioned, and (in the case of etched specimens) on the original α structure. This last, which is the structure of γ-iron, shows the characteristic twinned structure of this material.

The effects of strain indicated the three regions of temperature corresponding to the three allotropic forms of iron in a very definite manner. In the region of α-iron observation shows that on passing along the specimen in the direction of increasing temperature the amount of deformation, as evidenced by the number and depth of the slip-bands formed, increases steadily, but the slip-bands retain the curved and forked appearance characteristic of α-iron. The amount of deformation increases rapidly with increasing temperature until at a point of the specimen coinciding with the α/β transformation, the signs of deformation cease quite abruptly. For a short length of the specimen there are no slip-bands, and the material appears to have undergone no plastic deformation. On passing to still hotter portions of the specimen, slip-bands again appear, and when the region of γ-iron is reached the bands again become numerous, but now show

* A Paper read before the British Association (Section B), Sheffield Meeting, 1910.

the regular, rectilinear character and the characteristic features of twinned crystals, thus differing very strikingly from the slip-bands seen in α-iron.

The conclusions drawn from the observations here indicated are:—

1. That iron at temperatures up to 1100° C. behaves as a crystalline aggregate, and undergoes plastic deformation by a process of slip on the cleavage or gliding planes of its constituent crystal; this may or may not be accompanied by mechanical twinning.

2. That iron between the ordinary temperature and 1000° C. exists in three distinct modifications possessing widely different mechanical properties, and that the temperature-ranges in which these modifications exist are consistent with the identification of these three modifications with the α-, β-, and γ-forms of iron, according to the allotropic theory of Osmond and Roberts-Austen.

3. That β-iron, although existing at a higher temperature, is markedly stronger and harder than α-iron, and that the α/β transformation involves a volume-change.

4. That iron as found in approximately pure iron at high temperatures possesses the characteristic structure and some of the properties of "γ-iron" as found in certain alloy steels.

Incidentally, the demonstration of the real existence of a hard β-modification of iron at high temperatures serves to prove the correctness of the contention that the failure to harden pure iron by quenching is due to the difficulty of inhibiting the $\beta = \alpha$ transformation by rapid cooling, except in the presence of carbon. The observed power of β-iron to resist deformation at 800° C. under a stress which is sufficient to fracture the same section of α-iron at a temperature of 750° C., taken together with the powerful softening effect of a rise of temperature of 750°, serves to indicate that if β-iron could be preserved in existence at the ordinary temperature, it would possess a very high degree of hardness and strength, probably quite comparable with that of hardened steel.

EXTRACTION APPARATUS.

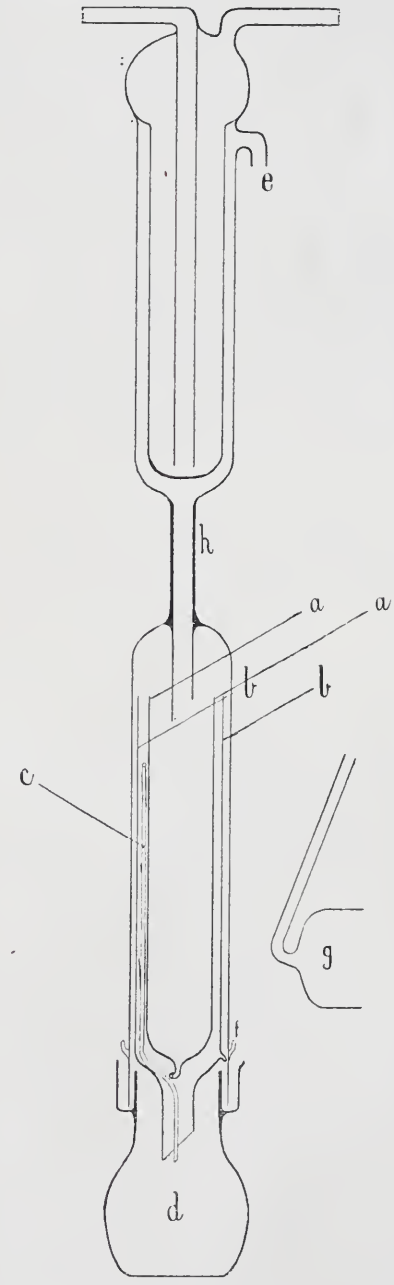
By G. S. WALPOLE, B.Sc., A.I.C.

The operation of extraction by means of the Soxhlet extractor and its more common modifications is attended by certain difficulties when an attempt is made to perform it under the conditions of quantitative analysis. It is generally desired to extract the material as completely as possible, and sometimes it is necessary to maintain the solvent perfectly dry. The apparatus, drawn to scale in section in the accompanying diagram, is the outcome of an attempt to do away completely with stoppers, both of rubber and cork, and their accompanying disadvantages; to increase the rate of extraction, by arranging that this shall take place at the boiling-point of the solvent; to prevent absolutely the entrance of water, and yet to keep the construction as simple as possible in order to minimise the cost and chance of breakage. In addition it will be observed that there are no ground-glass joints, so that all parts are interchangeable, any part of one extractor may be substituted for a corresponding part of any other extractor.

The several parts of the apparatus are—

1. A condenser and outer jacket all in one piece. At *f* are two projecting hooks of glass, which can take elastic bands passed round the flask *d*. These assist in holding the two parts together when the apparatus is in use. They were employed at first, but later were found to be unnecessary if the clamp and retort-stand holding the outer jacket were properly firm. The best place to clamp is the thick glass tube *h* joining the condenser to the outer jacket. The flask rests on the water-bath or other heating arrangement. At *e* a tube is sealed in, connecting the interior to the external air. A suitable drying attachment is fitted to this.

2. The flask *d*, contains the solvent. Several of these should be supplied. They can be tared if necessary. An additional ring of glass running round the neck holds sufficient mercury (not drawn in the diagram) to form an air-tight joint—a lip facilitates pouring the mercury out of this annular space.



3. A wide tube, labelled *b* in the diagram, having three projections near its lower constricted end. These rest on the edge of the neck of the flask. This supports the tube *a a*, and when the latter is dispensed with, as described below, can take a Soxhlet thimble.

4. An inner tube *a a*, best made of such dimensions that one of the stock sizes of Schleicher and Schüll's thimbles

just fits into it. At its lower end it is brought to a narrow constriction, and a capillary tube *c* is affixed and bent to form a syphon, as in the usual form of Soxhlet extractor.

5. The still-head *g*, by means of which the solvent may be recovered, leaving the extract in the tared flask.

During the actual process of extraction the liquid in *b b* is frequently seen to boil the whole time. It can always be arranged that either the flow of boiling solvent from the material undergoing extractlon is periodic, or else the flow is continuous through the completely covered material. Which of these two alternatives occurs depends on the tightness of packing of the thimble and its contents in the innermost tube. It is a matter of dispute which set of conditions brings about the better extraction. Sometimes, when extracting larger quantities of readily extracted material, it is convenient to dispense temporarily with the tube *a* and use tube *b*, packed at the lower end with a filtering material and filled with whatever is to be extracted. A small piece of platinum wire in *d*, to avoid "bumping," is used when necessary. Its weight is known, and one can allow for it accurately when weighing the extracts. For extractions lasting several days it is found convenient to use electric heaters made by placing nickel-wire coils of suitable length and fineness between two pieces of asbestos board. Regulation of these heaters is simply performed by using a piece of metal to short-circuit some of the turns as it is desired to raise the temperature.

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SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,*

INCLUDING PAINTS AND PAINT MATERIALS, INKS, LUBRICATING OILS, SOAPS, &c.

By PERCY H. WALKER.

(Continued from p. 107).

PAINTS (*continued*).

Coloured Pigments.

2. *Oxide and Earth Pigments.*—Iron oxide is extensively used as a paint. The native oxide naturally varies very much in its composition. In general, however, only the poorer grades of native hematite are used as paints. Artificial iron oxide pigments, made by calcining copperas, may be practically pure ferric oxide. Umbers, ochres, and siennas are earthy substances containing iron and manganese oxides and more or less organic matter.

The methods of analysis are very much the same as those for iron ores. It is generally sufficient to determine moisture, loss on ignition, insoluble in hydrochloric acid, ferric oxide, and manganese dioxide. If much organic matter is present, roast 2·5 grms. in a porcelain dish at a low temperature until all organic matter is destroyed, add 25 cc. of hydrochloric acid, cover with a watch-glass, and heat on the steam-bath for two hours; then add 10 cc. of sulphuric acid (1 : 1), evaporate, and heat until fumes of sulphur trioxide are evolved and all the hydrochloric acid is driven off. Cool, add 50 cc. of water, boil until all of the iron sulphate is dissolved, filter into a 250 cc. graduated flask, fill to the mark, mix, and take out a portion of 50 cc. for iron determinations. For the determination of iron reduce with zinc, titrate with standard potassium permanganate, and calculate to ferric oxide. For the determination of manganese transfer 100 cc. of the solution (corresponding to 1 grm.) to a 500 cc. flask, add sodium hydroxide solution until nearly but not quite neutral. Then add an emulsion of zinc oxide in water in slight excess, shake until all of the iron is thrown down, fill to the mark, mix, let settle, filter through a dry paper, and use portions of 100 cc. (corresponding to 0·2 grm.) for the manganese determination. Transfer to a 300 cc. Erlenmeyer flask, heat to boiling, titrate with standard permanganate. The flask must be shaken during the titration and some experience is necessary to determine the end-point, which is best seen by looking through the upper layer of liquid and observing when the pink tinge from the permanganate does not disappear on shaking. A standard potassium permanganate solution, the iron factor of which is known, may be used to determine manganese. The iron factor multiplied by 0·2952 gives the manganese factor. In some cases this method of attack will not separate all of the iron from the insoluble matter. In such a case the insoluble must be fused with a mixture of sodium and potassium carbonates, dissolved in water, evaporated with excess of sulphuric acid, filtered from the insoluble, and this solution added to the first one.

Another method is as follows:—Roast 5 grms. of the powder, digest with 25 cc. of hydrochloric acid, evaporate to dryness, moisten with hydrochloric acid, dissolve in water, filter, and wash the residue; ignite the residue in a platinum crucible, add sulphuric acid and hydrofluoric acid, drive off the latter, and heat until copious fumes of sulphuric anhydride come off. Add potassium hydrogen sulphate and fuse, dissolve in water, filter from any remaining insoluble (barium sulphate), unite the two solutions, make up to 500 cc., and use aliquots for the iron and manganese determinations. For the determination of iron place 100 cc. in a flask, add about 3 grms. of zinc, put a funnel into the neck of the flask, heat when the action slackens; if basic salts separate out add a few drops of hydrochloric acid. When all of the iron is reduced, add 30 cc. of sulphuric acid (1 : 2), and as soon as all of the zinc is dissolved and the solution is cool, titrate with potassium permanganate.

For the determination of manganese use 50 cc., evaporate to a very small bulk, add strong nitric acid and evaporate the hydrochloric acid; add 75 cc. of strong nitric acid, which should be free from nitrous acid, and 5 grms. of potassium chlorate, heat to boiling and boil for fifteen minutes; then add 50 cc. of nitric acid and more potassium chlorate. Boil until yellow fumes cease to come off, cool in ice-water, filter on asbestos and wash with colourless strong nitric acid; suck dry and wash out the remaining nitric acid with water, transfer the precipitate and the asbestos to a beaker, add a measured excess of standard solution of ferrous sulphate in dilute sulphuric acid, stir until all of the manganese dioxide is dissolved, and titrate the remaining ferrous sulphate with potassium permanganate. A ferrous solution of about the proper strength is made by dissolving 10 grms. of crystallised ferrous sulphate in 900 cc. of water and 100 cc. of sulphuric acid (specific gravity 1·84). This solution is titrated with standard potassium permanganate. The reaction taking place when the manganese dioxide acts on the ferrous sulphate is $MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + H_2O$. Hence the iron value of permanganate multiplied by 0·491 gives the value in manganese.

3. *Blue Pigments.*—There are two important blue pigments used in painting, Prussian blue and ultramarine. Of minor importance and very little used in paints for anything but artists' colours are cobalt blue and smalt.

(a) *Prussian Blue.*—Under the name Prussian blue are included all ferrocyanide blues such as Antwerp blue, Chinese blue, Turnbull's blue, &c. These blues are all ferric ferrocyanides, ferrous ferricyanides, or double iron potassium salts of hydroferrocyanic or hydroferricyanic acids. The analysis of these blues, as is generally the case with pigments, does not necessarily give results which can be used to grade samples, the strength and colour tests being most important. Most text-books say that Prussian blue is ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, but this substance is not known commercially. Commercial Prussian blue is a mixture of Williamson's blue, $KFe[Fe(CN)_6]$, with other iron-alkali cyanides and often with aluminium-iron cyanides, altogether a most complex substance (Parry and Coste, *The Analyst*, 1896, xxi., 225). (1) *Moisture.*—For the determination of moisture dry 2 grms. for two hours at 100° C. Dry blue should contain less than 7 per cent of moisture. (2) *Insoluble Impurities*,

—Ignite 1 grm. in a porcelain dish at a low temperature. The ignition should be carefully carried out at a temperature just high enough to decompose the last trace of blue, but not high enough to render the iron insoluble, or very difficultly soluble in hydrochloric acid. Cool, add 15 cc. of hydrochloric acid, digest for an hour on the steam-bath covered with a watch-glass, evaporate to a syrup, add water, boil, filter from the insoluble, wash, ignite, weigh, and determine the nature of the insoluble, probably barium sulphate. In pure Prussian blue solution should be complete. (3) *Total Iron.*—Decompose as in the foregoing determination, reduce, and determine the iron in the ordinary way. There should not be less than 30 per cent, calculated on the dry pigment. (4) *Total Nitrogen.*—Determine on a 1 grm. sample by the official Gunning method, digesting for three hours (U.S. Dept. Agr., Bureau of Chemistry, *Bull.* 107, Revised, p. 7). The percentage of Prussian blue may be obtained with sufficient accuracy for commercial purposes by multiplying the percentage of nitrogen by 4·4 and by multiplying the percentage of iron by 3·03. Eight samples of pure Prussian blue examined by Parry and Coste gave the mean results from which these factors are calculated. The table shows the accuracy with which these factors give the percentage of Prussian blue in the eight samples. (5) *Other Determinations.*—It is seldom worth while to make any further determinations.

Parry and Coste's Determination of the Percentage of Prussian Blue in the Dry Matter of Eight Samples.

No.	Factors.	
	Nitrogen × 4·4.	Iron × 3·03.
1.	94·69	94·63
2.	100·93	101·02
3.	107·58	109·71
4.	94·91	97·11
5.	98·95	94·84
6.	99·83	98·99
7.	100·80	102·47
8.	102·52	100·26

If desired, however, the iron and aluminium may be precipitated as hydrates by ammonium hydroxide and weighed together as oxides, and the aluminium obtained by difference after determining the iron volumetrically and calculating to ferric oxide. The filtrate from the iron oxide and alumina precipitate may be made up to a definite volume and one aliquot taken for the determination of sulphate and another evaporated with sulphuric acid, ignited, and weighed. Determine whether the alkali is sodium or potassium and subtract the alkali metal corresponding to the sulphate (SO_4) found. The remainder is double alkali iron ferrocyanide. Well-washed blues should be neutral in reaction. The red shade may be due to organic red. Test the solubility in alcohol, &c.

(b) *Ultramarine.*—Ultramarine is a compound of unknown constitution made by heating clay, soda, sulphur, and charcoal together. It appears to be complex silicate and sulphide of aluminium and sodium. Ultramarine may be readily distinguished from Prussian blue by being dissolved in hydrochloric acid with the evolution of hydrogen sulphide. It can not be mixed with lead pigments on account of the sulphide present. Good ultramarine gives little tarnish on polished copper. An analysis is of little value, but if desired may be conducted as follows:—(1) *Moisture.*—Dry 2 grms. for two hours at 105° C. (2) *Silica.*—Treat 1 grm. with 20 cc. of hydrochloric acid (1 : 1) in a covered dish, heat until decomposed, remove the cover and evaporate to dryness on a water-bath, moisten with hydrochloric acid and again heat to dryness, add 1 cc. of hydrochloric acid, let stand five minutes, add hot water, filter, and wash the insoluble. If great accuracy is desired, evaporate the filtrate to dryness, take up with hydrochloric acid and water, filter, and add the precipitate to the main insoluble. Ignite the insoluble, weigh as silicon dioxide, and test the purity with hydrofluoric acid. (3) *Aluminium.*—Determine the aluminium in the filtrate from the silicon dioxide by precipitating with ammonium hydroxide, igniting, and weighing as aluminium oxide. (4) *Soda.*—Add sulphuric acid to the filtrate from aluminium hydroxide, evaporate to dryness, ignite, and weigh as sodium sulphate (Na_2SO_4). Calculate to sodium monoxide (Na_2O). If calcium is present it should be precipitated with ammonium oxalate in the filtrate from aluminium hydroxide, ignited, and weighed as calcium oxide, and the soda determined in the filtrate from the calcium oxalate, as described previously. (5) *Sulphur.*—Mix 1 grm. of ultramarine with 4 grms. of sodium carbonate and 4 grms. of sodium peroxide in a nickel crucible, cover with about a grm. of sodium carbonate, fuse, using an aluminium or asbestos shield to prevent the sulphur from being taken up from the gas. Dissolve the fused mass in water, making acid with hydrochloric acid; there is no insoluble residue. Precipitate with barium chloride and determine total sulphur by weighing the barium sulphate. (6) *Sulphur as Sulphate.*—Weigh 1 grm. in a beaker, add water, then hydrochloric acid, boil until the hydrogen sulphide is expelled, then add barium chloride, and determine the sulphur as usual by weighing the barium sulphate. (7) *Sulphur as Sulphide.*—Subtract sulphur as sulphate from the total sulphur. Pure ultramarine will generally have about the following composition:—

	Per cent.
Silicon dioxide (SiO_2)	39 to 43
Alumina (Al_2O_3)	24 to 30
Sodium monoxide (Na_2O)	17 to 21
Sulphur (S)	10 to 16

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académié des Sciences. Vol. cl., No. 26, June 27, 1910.

Effect of a Red-heat on Formaldehyde.—Armand Gautier.—When formaldehyde vapour and hydrogen are led through a porcelain tube heated to 800° decomposition occurs according to the equation $CH_2O = CO + H_2$. The analysis of the gaseous products shows that 48 per cent of carbon monoxide are formed and 51 per cent of hydrogen, together with traces of methane. No carbon nor tarry matter remains in the tube. More energetic reducing agents, *e.g.*, iron, bring about the same reaction, although rather more methane is formed.

Atomic Weight of Radium Emanation.—A. Debierne.—Already noticed.

Duration of Emission of Spectral Rays by Luminous Vapours in the Electric Spark.—G. A. Hemsalech.—When a spark passes between metallic electrodes a luminous vapour is projected into the surrounding space, and at the end of a certain time loses its power of emitting spectral rays. The length of this period of time in the case of 200 spectral rays of iron seems to be proportional to the intensities, although there are some exceptions to this rule. The duration of the emission increases with the capacity of the condenser.

Potassium Rays.—E. Henriot.—The author has already shown that the emission of radiation is a normal property of a salt of potassium. The activity of a salt is directly proportional to the amount of metal it contains. When a phenomenon is atomic its intensity is independent of the temperature, and this is true of potassium radiation between 14° and 140°. The radiation from all salts is of the same nature, has the same power of penetration, and is spontaneous.

Action of Hydrogen on Sulphur Chloride and Thionyl Chloride under the Influence of the Silent Discharge.—A. Besson and L. Fournier.—Under the action of the silent discharge hydrogen decomposes sulphur

chloride at 150—170°, setting free sulphur. At temperatures slightly above the melting-point the chloride is decomposed into the dichloride SCl_2 and sulphur by the action of heat alone. When thionyl chloride and pure dry hydrogen are subjected to the action of the silent discharge sulphur and sulphur chloride are formed.

Hydrogenation of Acetylenic Compounds. — M. Lespieau.—By the aid of the catalytic action of platinum black the mono- and diacetylene glycols, such as $CH_2OH—C{\equiv}C—CH_2OH$, can be hydrogenated to form the tetramethylene glycols, *e.g*, $CH_2OH–CH_2–CH_2–CH_2OH$. Similarly, $CH_2OH—C{\equiv}C-C{\equiv}C—CH_2OH$ yields hexamethylene glycol, $CH_2OH\cdot CH_2—CH_2—CH_2—CH_2OH$.

Electrical Properties of Aluminium-Silver Alloys. —Witold Broniewski.—The author has studied the electrical properties of alloys of aluminium and silver, and has expressed the results in a series of graphical representations. These alloys are hard, do not readily undergo alteration, and would be found very useful from a technical point of view. From the curves it appears that two well-defined compounds, $AlAg_3$ and Al_2Ag_3, exist.

MISCELLANEOUS.

Iron and Steel Institute (Buxton Meeting).—Arrangements have been made to hold the Autumn Meeting of the Iron and Steel Institute at Buxton, on Monday, Tuesday, Wednesday, Thursday, and Friday, September 26th, 27th, 28th, 29th, and 30th, 1910. The following papers have been offered for reading :—

" Electric Steel Refining," by D. F. Campbell (London).
" The Hanyang Iron and Steel Works," by G. Chamier (Hankow, China).
" Manganese in Cast-iron and the Volume Changes during Cooling," by H. I. Coe, B.Sc. (Birmingham).
" Sulphurous Acid as a Metallographic Etching Medium," by E. Colver-Glaubert (Berlin) and S. Hilpert (Charlottenburg).
" Theory of Hardening Carbon Steels," by C. A. Edwards (Manchester).
" Influence of Silicon on Pure Cast-iron," by A. Hague, B.Sc. (Birmingham) and T. Turner, M.Sc. (Birmingham).
" Preparation of Magnetic Oxides of Iron from Aqueous Solutions," by S. Hilpert (Charlottenburg).
" Manufacture of Rolled ' H ' Beams," by G. E. Moore (Loughborough).
" Utilisation of Electric Power in the Iron and Steel Industry," by J. Elink Schuurman (Baden, Switzerland).
" Briquetting of Iron Ores," by C. de Schwarz (Liége).
" Some Experiments on Fatigue of Metals," by J. H. Smith (Belfast).

Annual Exhibition of the Royal Photographic Society of Great Britain.—The Annual Exhibition of photographs by the Royal Photographic Society is held this year at the Royal Water Colour Society's Gallery in Pall Mall. The Exhibition, which remains open till September 16th, is divided into four sections :—Pictorial, Colour Photography, Natural History Photography, and Scientific Applications of Photography. The first and second of these sections are in the principal gallery, the drab and dull crimson drapery of which harmonises well with the monochrome prints. The third and fourth sections are hung in the two smaller rooms looking over Pall Mall. In previous years the exhibits of apparatus and materials by the principal trade firms, and examples of professional work occupied a considerable portion of the space at the New Gallery, but are absent from Pall Mall, the whole of the available space being required for the competitive exhibits. A glance at the catalogue shows that practically the same number of photographs as last year have been accepted in the pictorial section, and that without overcrowding the walls. Although no one picture stands out in marked contrast to its neighbours, the general standard is undoubtedly high, and it is worthy of note that the exhibition is supported by most of the best known workers in all countries, maintaining the international character which has long been a feature of the Society's exhibitions. This year, as last, the Society has asked that the processes by which the pictures are produced should be stated, and a fair proportion of the exhibitors have responded to the call, and it is possible to gauge with some approach to accuracy the extent to which these processes rise and fall in the estimation of the best workers. Bromide prints, which suffered a slight eclipse last season, take the premier position this year ; the recently invented bromoil process is not far behind in numbers, and if we add those prints produced by the older oil process the two combined take the first place. Platinum prints are next on the list, having assumed the place formerly held by gum bichromate, and with the exception of some little used methods the beautiful carbon process is still lowest on the list. There are few examples of photographs produced in colour by the oil process, but these few are remarkably good, and further advance may be expected as workers acquire facility in the use of their materials. The section is strong in quality and varied in subject, and the growing tendency to work in a higher key than in the past give to the walls a brighter and more cheerful aspect than has been the case of late years. The narrower frames and lighter tinted mounts have also the effect of removing from photography the reproach of being the dismal art. The collection of Autochrome and other transparencies in colour is a small one, some eighty in all, including the scientific examples ; but the section has benefited by rigorous selection, and every example is worthy of close examination. The Autochrome, as was to be expected, far outnumber the others, but there are one or two examples of the Dufay Dioptichrome process which promise well for this new claimant for popularity. A few transparencies by the Sanger Shepherd or triple film process are to be seen with other technical subjects in the scientific section. The Natural History Section, though not large, is interesting in character and varied in subject, each exhibit having some peculiarity which warrants its inclusion. The Scientific Section has also been subject to stringent selection, and consists chiefly of photomicrographs and radiographs, although some stellar and cloud studies are also to be seen. The exhibition is open morning and evening, and the lantern lectures—which are a popular feature in the Society's work—are delivered on Mondays, Wednesdays, Thursdays, and Saturdays.

Sir John Cass Technical Institute.—The new session of this Institute, which is especially devoted to technical training in experimental science and in the artistic crafts, will commence on Monday, September 26th. The instruction includes Physics and Mathematics, Pure and Applied Chemistry, and Metallurgy. In each subject graded curricula of study extending over several years are provided both for those engaged in chemical, electrical, and metallurgical industries, and for students preparing for London University degrees. In addition, several special courses of instruction are given, amongst which we note the following :—In the department of Physics and Mathematics courses on " Integral and Differential Calculus " for science students, and on " Conduction in Gases and Radio-activity." In the Chemical department there is a well-arranged curriculum for those engaged in the Fermentation industries, which includes lectures and laboratory instruction in " Brewing and Malting " and on the " Micro-biology of the Fermentation Industries," and a series of courses on " Liquid, Gaseous, and Solid Fuel," which comprise a course of lectures and laboratory work on " Fuel Analysis " and on " Technical Gas Analysis." In the Metallurgy department, in addition to the ordinary courses of instruction in general metallurgy, special courses of an advanced character are provided on Gold, Silver, and allied metals, on Iron and Steel, and on Metallography. It is also of interest to note that included amongst the Language Classes is a course on Scientific and Technical German.

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UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Intending Students (Internal and External) should obtain the "Regulations and Courses" from the Registrar, University of London, South Kensington, S.W.

Several valuable Scholarships and Exhibitions are available to students.

Intermediate Examination in Science.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate is admitted to this Examination unless he has passed, or been admitted under the Statute referred to above as exempt from, a Matriculation Examination not later than that of the preceding January.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. Examination.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry candidates are required to show a general acquaintance with General Theoretical Chemistry, Chemistry of Carbon Compounds, Physical Chemistry, and History of Chemistry since the time of Boyle.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

Doctor of Science.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Preliminary Scientific (M.B.) Examination.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, F.R.S.

Lees Reader in Chemistry—H. Brereton Baker, M.A., D.Sc., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities and other persons suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. Watts, M.A., and J. E. Marsh, M.A., F.R.S., N. V. Sidgwick, M.A., A. F. Walden, M.A., B. Lambert, M.A.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

There are also laboratories which specialise in different parts of the subject:—*Physical Chemistry*, Balliol and Trinity College Laboratory: D. H. Nagel, M.A., H. B. Hartley, M.A. *Inorganic Chemistry*, Christ Church Laboratory: Dr. Baker, W. Akers, B.A. *Quantitative Analysis*, Magdalen College Laboratory: J. J. Manley, M.A. Jesus College Laboratory: D. L. Chapman, M.A. Queen's College Laboratory: Rev. H. B. Cronshaw, M.A.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—William J. Pope, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

Goldsmiths Reader in Metallurgy—Charles T. Heycock, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University, either by examination or by presentation of a thesis describing original research.

Facilities for research work are provided both in the Chemical Laboratories and in the Metallurgical Laboratories.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratories of the University are open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures is published annually, in June, in a special number of the

Cambridge University Reporter, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrary, Cambridge, from the *Cambridge University Calendar*, or from the "Students' Handbook to Cambridge."

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Professor of Applied Chemistry—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C S.

Junior Demonstrators—W. R. G. Atkins, B.A., T. A. Wallace, B.A.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on October 1st. Lectures will commence about November 1st.

The Laboratories and the Lectures ofthe Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.
4. *Agricultural Chemistry.*—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins early in April and terminates about the end of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. The Foundation Scholars receive £20 per annum, they have free commons, and their chambers for half the charge paid by other students; their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(UNIVERSITY OF LONDON).

Senior Professor of Chemistry—J. M. Thomson, LL.D. F.R.S.

Professors—Herbert Jackson, F.C.S., and P. H. Kirkaldy, F.C.S.

Lecturer and Demonstrators—H. L. Smith, B.Sc., S. W. Collins, B.Sc., and L. E. Hinkel.

The Academical Year consists of Three terms. The days fixed for the commencement of Terms in 1910-1911 are Oct. 5, Jan. 18, and May 3.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Fees.—Chemistry: Winter Session, £5 5s.; Summer Session, £3 3s. Practical Chemistry: Winter Session, £8 8s.; Summer Session, £4 4s. Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; One Term, £10 10s.; Two Terms, £18 18s.; Three Terms, £26 5s. Three days a week: One month, £2 12s. 6d.; One Term, £6 6s.; Two Terms, £11 11s.; Three Terms, £15 15s.

For fuller details the separate Syllabuses provided for each class should be consulted.

METALLURGY.

Professor—A. K. Huntington, A.R.S.M, F.I.C., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Fee, £3 3s. for the Course.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, LL.D., F.R.S.

For particulars apply to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

(UNIVERSITY OF LONDON).

Professors—Sir William Ramsay, K.C.B., LL.D., F.R.S. (Inorganic and Physical Chemistry); J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry).

Assistants—R. W. Gray, Ph.D.; S. Smiles, D.Sc.; N. T. M. Wilsmore, M.Sc.; Katharine A. Burke, B.Sc.; W. C. McC. Lewis, D.Sc.

The Session is divided into three Terms, as follows:—First Term, from October 3 to December 21; Second Term, from January 10 to March 31; Third Term, from May 2 to July 6.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Thursday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

This Course treats of the chief physical and chemical

characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

In this Course the physical principles bearing on Chemistry are first discussed, and the Chemistry of the Elements and their compounds is treated in considerable detail, under the headings—Elements; hydrides, halides, oxides, sulphides, &c., borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and on Wednesdays at 11, on the chief types of Carbon Compounds.

Fees: Course, £7 7s.; First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Course of Physical Chemistry.

October to February: Tuesday and Thursday at 9. January to June: Tuesday and Thursday at 11.

The Principles of Chemistry will be specially considered, comprising the Atomic Theory, Chemical Classification, the Periodic Law, Thermal Chemistry, Dissociation, the Application of Physical Methods to the Solution of Chemical Problems, and the influence of Mass and Temperature on the progress of Reactions. Special attention is paid to the most recent Chemical Theory researches.

Fees:—Courses, £5 5s.; Term, £2 2s.

Senior Course of Inorganic Chemistry.

This Course will begin about the middle of February; Tuesday and Thursday at 9. Fee, £3 3s.

Organic Chemistry.

Mon. at 12, Wed. and Fri. at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the Course of Physical Chemistry, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

Emeritus Professor—Sir W. A. Tilden, D.Sc., F.R.S.

Professor and Director of the Chemical Laboratories—Sir T. E. Thorpe, C.B., F.R.S., &c.

Assistant Professors—M. O. Forster, Ph.D., D.Sc., F.R.S.; G. T. Morgan, D.Sc., A.R.C.S.; J. C. Philip, M.A., Ph.D., B.Sc.

The Imperial College of Science and Technology, incorporated under the Royal Charter of July 8, 1907, is an institution or group of associated colleges with its principal seat at South Kensington.

The purposes of the Imperial College are to give the highest specialised instruction, and to provide the fullest equipment for the most advanced training and research in various branches of science, especially in its application to industry; and to do all and any of such things as the Governing Body consider conducive or incidental thereto, having regard to the provision for those purposes which already exists elsewhere.

For these purposes, the Governing Body, subject to the provisions of the Charter, are to carry on the work of the Royal College of Science, and the Royal School of Mines, and may establish Colleges and other Institutions or Departments of Instruction. Any Institution or Department so established, and, subject to the conditions of the Charter, the Central Technical College of the City and Guilds of London Institute, are to be integral parts of the Imperial College; and the Central Technical College is to be called and known in future as the City and Guilds College.

Subject to agreement with the authorities of any College or other Institution, the Governing Body may by resolution recognise that College or Institution or any Department thereof, as being in association with the Imperial College for all or any of the purposes of the Charter, but no such resolution is to be valid or operative until allowed by the King in Council.

The Charter further provides that the Imperial College shall be established in the first instance as a School of the University of London. Students of the Imperial College who have matriculated at the University of London may therefore proceed to the Science degree of the University as "Internal Students."

Attention is particularly directed to the conditions of admission and to the extended facilities for Research Work.

The ordinary courses of instruction are planned so as to extend over four years, and are generally similar for all divisions during the first year, and to a less extent during the second year, after which they are specialised according to the particular course which the student is taking.

The following Diplomas have been awarded in the past to Students of the several constituent Colleges:—

The Associateship of the Royal College of Science (A.R.C.S.) in one or more of the following divisions:—Mechanics, Physics, Chemistry, Botany, Zoology, Geology.

The Associateship of the Royal School of Mines (A.R.S.M.) in one or more of the following divisions:—Metallurgy, Mining.

The Associateship of the City and Guilds Institute (A.C.G.I.) in one or more of the following divisions:—Chemistry, Engineering (Civil and Mechanical), Engineering (Electrical).

The instruction in Chemical Science embraces:—

1. Courses of lectures on the laws and general principles of Chemistry, including the special study of compounds of carbon, usually called "Organic Chemistry"; on the theory and methods of Chemical Analysis; and on Physical Chemistry.

2. A systematic Laboratory course for the practice of Qualitative and Quantitative Analysis.

An examination will be held at the end of each course of instruction, and all candidates for a Diploma in Chemistry will be required to qualify in each successive stage.

A Laboratory course is provided for advanced students desirous of acquiring a knowledge of the methods employed in research and for the prosecution of Chemical Investigations.

Full details can be obtained from the College Calendar, published by Eyre and Spottiswoode (or through any bookseller), price 6d.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The 68th Session will commence on Oct. 5, 1910.

Professors—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C., F.R.S. (Dean); Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the Conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance at the Course of Pharmacy is also accepted by the Conjoint Board.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Director of the Edward Davies Chemical Laboratories and Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Assistant Lecturers and Demonstrators—A. Brooke, Ph.D. (Strass.), and T. C. James, M.A. (Cantab.), B.Sc.

Student Assistant—Miss M. K. Turner, B.Sc. (Lond.).

Lecturer in Agricultural Chemistry—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Oct. 4th, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1910-1911, Course B). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m., and from 2 to 6 p.m., except on Saturdays. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 20, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D, F.I.C. Assistant Lecturer and Demonstrator, Alice E. Smith, B.Sc. Assistant Lecturer in Agricultural Chemistry, R. Gaunt, Ph.D, M.Sc. Junior Demonstrator, J. O. Hughes, B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc. Assistant Lecturers and Demonstrators, A. H. Ferguson, B.Sc., and W. E. Williams, B.Sc.

The Session opens October 4th, 1910. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s. Advanced Lectures on Organic Chemistry, £1 1s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical operations and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and by the Conjoint Boards of the Royal Colleges of Surgeons and Physicians, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Universities mentioned, the First Examination for Medical Degrees of the University of London, and of Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Demonstrator—R. D. Abell, D.Sc., Ph.D., F.I.C., F.C.S.

Professor in Metallurgy—A. A. Read, M.Met., F.I.C., F.C.S.

The Session commences October 4th, and terminates on June 30th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 30 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s.

The Intermediate Course consists of about 80 lectures; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science (Part I.) of the University of London. Fee, £4 4s.

The Senior Course consists of about 80 lectures on Inorganic Chemistry; Fee, £3 3s.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in April, and the annua examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY OF BRISTOL.

Department of Chemistry.

Alfred Capper Pass Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturers—O. C. M. Davis, B.Sc., M.Sc., F.I.C.; F. W. Rixon, M.Sc., PhD.

Lecturer in Inorganic and Physical Chemistry—James W. McBain, M.A., Ph.D.

Lecturer in Bio-chemistry—Max. Nierenstein, Ph.D.

Lecturer in Agricultural Chemistry—C. T. Gimingham, F.I.C.

Lecturer in Hygienic Chemistry—F. Wallis Stoddart, F.I.C.

Lecture Assistant—J. H. Sturgess.

The session 1910-1911 commences on October 3, and ends on July 1, 1911.

The new wing of the University Buildings in Tyndall's Park, containing the departments of Chemistry and Physiology, will be opened on October 1; they are being completed at a cost of about £50,000 from the designs of Messrs. Oatley and Lawrence. The Chemical Department provides accommodation for 200 students, and laboratories for work in specialised branches of Chemistry have been designed and equipped with apparatus of the most modern type. All the laboratories are supplied with electric wiring for experimental purposes, and currents of any desired voltage up to 250 volts at 50 ampères from dynamo or storage cells may be obtained throughout the Department. Higher voltages and currents are available in special laboratories, for Physical Chemistry and Electrometallurgy. Special facilities are afforded to those who desire to carry out research or to study Chemistry as applied to the different processes employed in the arts and manufactures; and a laboratory for Bio-chemistry has been specially designed for the investigations of problems on Biological lines.

Day Lectures.

General Courses.—(A) Introductory—Three Lectures and two afternoons Laboratory per week during Session. (B) General Inorganic Chemistry—Three lectures per week during Session and Laboratory work. (C) General Organic Chemistry—Three Lectures per week during one Session and Laboratory work. Physical Chemistry—Two Lectures per week for two Sessions and Laboratory work.

The Laboratories are open daily from 9 to 5 except on Saturdays, when they are open for Senior Students only.

Courses for Graduation.—Intermediate Science—Course B and one day Laboratory per week. *Pass Degree*—Course C and D, and at least one day Laboratory per week during two Sessions. The Chemical Society must be attended during the second and third years, and one or more of the Special Courses arranged for Honours Students. *Honours Degree*—During the first year in the Honours School Courses C and D, and the second and third Course D, and one or more of the following Special Courses as directed, *e.g.*:—Organic Chemistry, Physical Chemistry, Mathematical Chemistry, Advanced Inorganic Chemistry, Applied Electro-chemistry, some part of Bio chemistry, Analysis of Foods and Drugs.

The Colloquium and meetings of the Chemical Society must be attended during each Session.

Colloquium.—A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various developments of Chemistry. Honours Students attend, and others interested are invited to do so.

Extract from Regulations as Regards Fees.

1. Registration Fee 7s. for a single Course; £1 1s. shall cover a perpetual registration for any number of Courses.

2. Inclusive Fee for an entire curriculum for degree of B.Sc., whether "Pass" or "Honours," shall be £21 a year

3. The Fees for separate Courses of Lecturers in Faculty of Science shall be at the rate of £1 1s. per term, or £2 2s. a year for each hour per week for which the Course in question is offered.

The Fees for separate Laboratory practice and instruction in the Faculty of Science shall be at the rate of £2 2s. per term for each day in the week for which admission in the Laboratories is sought, with a minimum of £3 3s. in each particular case.

Evening Lectures.

The Laboratories are opened from 6.30 to 9 30 p.m. on Tuesday during the Autumn and Spring Terms. Course A will be given on Wednesday at 8 to 9, and Course B on Friday at 8 to 9 p.m. during these Terms. The Lectures and Laboratory work in Course A will be similar to that given to Intermediate Students in the Faculty of Science, and that given in Course B to one of those given to Students studying for the Final Degrees in that Faculty.

Extract from Regulations as Regards Fees for Evening Students.

1. For Evening Students who enter on a curriculum for a Degree the Registration Fee shall be 5s., for a curriculum for a Certificate, unless the Student has matriculated, the fee shall be 10s. 6d.

2. Unless in any case otherwise prescribed, the Fees for Evening Classes in the Faculties of Arts and Science shall be 10s. 6d. for two terms, or for one term's attendance.

All communications to the University to be addressed to the Registrar. Information concerning Courses or

Laboratory work in the Department of Chemistry may be obtained from the Professor.

The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, mining, or motor car engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the University into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the University. Several Scholarships are tenable at the University.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

Chemistry.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.
Lecturers—H. A. M. Borland, A.R.C.S.; E. E. Elt, B Sc.
Demonstrator—E. H. T. Parker.
Assistant in Chemical Laboratory—B. Drake.

In consequence of the foundation of the University of Bristol, the College now restricts its work to Applied Chemistry in the daytime; Pure Chemistry is taught at the University College. The Engineering work of the University College has, on the other hand, been transferred to this College.

The College Evening Classes commence on Monday, October 3.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (1d. each).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S., F.I.C.
Assistant Lecturers and Demonstrators—Alex. Findlay, M.A., D.Sc., Ph.D.; Hamilton McCombie, M.A , Ph.D., B.Sc., A.R C.S., A.I.C.; C. K. Tinkler, D.Sc., and T. J. Murray, Ph.D., M.Sc.
Professor of Metallurgy—Thomas Turner, M.Sc., A.R.S.M.

The Session will be opened on October 3rd, 1910.

The Chemical Department is now housed in the new University buildings at Bournbrook.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Three hours weekly during the Winter and Spring terms. Mondays, Wednesdays, and Thursdays at 9.30 a m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9 30 to 10 30 a.m. Fee, £1 11s. 6d.

Second Year.—Advanced Organic Chemistry.—This course extends over two years, and is divided into two parts:—(*a*) Carbon Compounds of the Fatty Series; (*b*) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *General and Physical Chemistry.*—This course will deal in outline with the more recent developments of Theoretical Chemistry. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General and Physical Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Fourth Year.—For students preparing for the B.Sc. degree with Honours in Chemistry.

Practical Chemistry.

The instruction in Practical Chemistry extends over four years in the case of the Honours Degree. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6¼

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. Gardner, M.Sc.

Department of Chemistry and Dyeing.

Professor of Chemistry and Dyeing—W. M. Gardner, M.Sc.
Assistant Professor of Chemistry—B. North, A.R.C.Sc. (Lond).
Lecturers in Chemistry—L. L. Lloyd, Ph.D.; H. H. Hodgson, M.A., B.Sc., Ph.D.; S. F. Stell, F C.S.
Demonstrators in Chemistry—A. E. Findley, B.Sc.; S. M. Sutcliffe, F.C.S.
Lecturer in Physics—J. A. Tomkins, A.R.C.Sc. (Lond.).
Demonstrator in Physics—F. Harcourt, B.Sc.
Lecturer in Dyeing—A. B. Knaggs, F.C.S.
Demonstrator in Dyeing—T. Brooke.
Lecturer in Gas Manufacture—W. Cranfield.
Lecturer in Botany, Biology, and Pharmacy—W. West, F.L.S., Past Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided—

I. *General Chemistry Course*, extending over four years, and including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Special Courses for Graduates in Chemistry, and for Drysalters, Colour Merchants, &c.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.), London.*—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Demonstrator—M. Kershaw, B.A., Ag.Dip. Cambs.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc.

Lecturer on Physical Chemistry—H. M. Dawson, D.Sc., Ph.D.

Assistant Lecturers and Demonstrators—W. H. Perkins, B.Sc.; W. Lowson, B.Sc., F.I.C.

Demonstrators—H. Calam, M.Sc.; A. T. King, B.Sc.; J. Marshall, B.Sc.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. Advanced Inorganic Chemistry.—Metals. Monday Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Advanced Inorganic Chemistry.—Non-metals. Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.

5. Honours Courses.—(*a*) Organic Chemistry: Monday, Wednesday, and Friday at 12 noon in the First and Second Terms; fee, £2 12s. 6d. (*b*) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £1 11s. 6d. (*c*) Physical Chemistry: Monday, Wednesday, and Friday at 9 30 a.m. in the Second and Third Terms; fee, £2 12s. 6d. (*d*) Electro-chemistry: One hour weekly; 31s. 6d.

6. Chemistry of Food and Drugs.—Special class for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £2 2s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session.—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from April to June. Fee, £5 5s.

Tinctorial Chemistry and Dyeing Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Chemist—A. G. Perkin, F.R.S. F.I.C.

Assistant Lecturer—G. H. Frank, B.Sc.

Demonstrator—A. Woodhead, B Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, colour manufacture, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c., or in the manufacture of coal-tar products and dyestuffs.

Leather Industries Department.

Professor—H. R. Procter, M.Sc., F.I.C.

Assistant Professor—E. Stiasny, Ph.D.

Demonstrator—Harold Brumwell.

Research Assistant—A. Seymour-Jones, B.Sc.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies three years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture at the University Farm.

Fuel and Metallurgical Department.

Professor—William A. Bone, D.Sc., Ph.D, F.R.S.

Demonstrator and Research Assistant—H. H. Gray, B.Sc.

The Courses extend over two, three, or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by-product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores,

will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the microstructure, physical properties, and heat treatment of steel and other industrial alloys.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £100 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Inorganic Chemistry—E. C. C. Baly, F.R.S.

Professor of Physical Chemistry—F. G. Donnan, M.A. Ph.D.

Professor o Bio-chemistry—Benjamin Moore, M.A., D.Sc.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy — Guy D. Bengough, M.A., A.R.S.M.

Assistant Lecturers and Demonstrators—H. Bassett, D.Sc., Ph.D., Francis W. Kay, M.Sc., Ph.D.; A. Rule, M.Sc., Ph.D.; R. E. Slade, M.Sc.; J. Smeath Thomas, M.Sc.

The Session commences October 4th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Introductory Course, including the principles of Organic, Physical, and Bio-chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £6.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £2 10s.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Organic (Honours). Fee, £4.

Course F.—Physical Chemistry. Fee, £3.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—History of Chemistry and Chemical Philosophy. Fee, £2.

Course J.—Applied Inorganic Chemistry, including Metallurgy. Fee, £2.

Course K.—Applied Organic Chemistry. Fee, £2 10s.

Course L—Applied Electro-chemistry. Fee, £2 10s.

Pass and Honours Courses will also be given in Bio-chemistry.

Research students carrying out research work pay a fee of £3 per annum.

The Inorganic and Organic Chemical Laboratories provide accommodation for every kind of work and research in inorganic and organic chemistry and in metallurgy. There is also a laboratory devoted to spectroscopic work and research.

The Muspratt Laboratories of Physical Chemistry and Electro-chemistry adjoin the main chemistry buildings, and, owing to their full equipment, offer every opportunity or all manner of work and research in these subjects.

The Bio-chemical Laboratory is also separately housed, and provides facilities for work and research.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

Per Week	One Term, Three Months.	Three Terms One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

D.P.H. Course (see special syllabus).

Course for Dental Degree and Diploma (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sir John Willox Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1911, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the College Secretary not later than November 15. The Sheridan Muspratt Chemical Scholarship, on similar lines, is open for competition. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes on Metallurgy will be held during the winter.

Prospectuses containing particulars may be obtained from the Registrar, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.
(IN THE UNIVERSITY OF DURHAM).

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturers in Chemistry—F. C. Garrett, D.Sc., F.C.S., and J. A. Smythe, D.Sc., Ph.D., F.C.S.

Assistant Lecturer and Demonstrator—A. A. Hall, M.Sc., Ph.D.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

Assistant to Lecturer in Agricultural Chemistry—J. Potts, B.Sc.

Demonstrator—Vacant.

First Year Courses.—Division I.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 5th. Fee, £3 10s. for the Session.

Division II. Similar to Division I., but modified to meet requirements of Students for Degrees in Engineering and Mining. Mondays 12 to 1, Tuesdays and Thursdays 10 to 11. Fee, £3 10s. for Session.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 4th. The class for Inorganic Chemistry meets at 3 p.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Prof. Louis, M.A., D.Sc., F.I.C., F.G.S.; Demonstrator, H. Dean, M.Sc., A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week £5 10s. per term, £15 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must have passed the University Matriculation Examination.

Matriculation Examination.—In order to enter on a course of study for a Degree a student must have previously satisfied the Examiners in the following subjects:—(1) English, (2) English History, (3) Mathematics, (4) three of the following subjects, of which one must be a language:—(*a*) Religious Knowledge, (*b*) Latin, (*c*) Greek, (*d*) French, (*e*) German, (*f*) some other language to be approved, (*g*) Experimental Science or Physics or Chemistry, (*h*) Botany or Zoology, (*i*) Mechanics, (*k*) Extra Mathematics, (*l*) Geography.

(i.). Candidates for degrees in Arts, who do not offer Latin in their Matriculation Examination or in the equivalent accepted as exempting therefrom, will be required to pass in Latin at a subsequent examination before entering upon the Arts course.

(ii.). Candidates for degrees in Engineering (Civil, Mechanical, and Electrical) and in Naval Architecture will be required to take the following subjects from the list:—(1) English; (2) English History; (3) one of four languages—Latin, Greek, French, German; (4) Experimental Science; (5) Extra Mathematics; (6) Geography.

(iii.). Foreign Students may be exempted from the Matriculation Examination on report from the Board of Professors of Armstrong College, that they have already passed an examination equivalent to the Matriculation Examination of the University, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

(iv.). Students from Oriental countries may be exempted from the Matriculation Examination on report from the Professors of Armstrong College that they have received such an education in their own country as will enable them to profit by University study, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—Every candidate for the Bachelorship in Science will be required to satisfy the examiners in Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the third year in an examination in one chief and two auxiliary subjects. For details of the subjects the College Calendar should be consulted. Candidates may qualify for the degree of B.Sc. by attending special courses in Agriculture, Engineering, and Mining. and passing the several examinations.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, September 29th, 1910. Candidates should send in their names to the Secretary on or before September 11th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing October 3rd. Candidates should send in their names to the Secretary on or before September 24th.

THE UNIVERSITY OF MANCHESTER.

Professor of Chemistry and Director of the Inorganic Laboratories—Harold B. Dixon, M.A., M.Sc, Ph.D, F.R.S.

Professor of Chemistry and Director of the Organic Laboratories—W. H. Perkin, Ph.D., D.Sc., F.R.S.

Senior Lecturers and Demonstrators—Arthur Lapworth, D.Sc., F.R.S.; C. Weizmann, Ph.D., D.Sc.; Norman Smith, D.Sc.; and E. C. Edgar, D.Sc.

Assistant Lecturers and Demonstrators—Robert Robinson, D.Sc.; A. Holt, M.A., D.Sc.; F. P. Burt, B.Sc; F. R. Lankshear, B.A.

Professor of Metallurgy—H. C. Carpenter, M.A., Ph.D.

Demonstrator and Research Fellow in Metallurgy—C. A. Edwards (Carnegie Scholar of the Iron and Steel Institute).

Lecturer in Electro-Chemistry—J. N. Pring, D.Sc.

The Session begins October 4, 1910.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during the Lent Term.

These courses are intended for Students commencing the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Wednesdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Each Course, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: Two hours per week during the Michaelmas Term.

B.Sc. with Honours in Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

The Research Laboratories for Inorganic, Organic, and

Physical Chemistry, and for Metallurgy, are open to graduates and other advanced students.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A., or to the Directors of the Laboratories.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; G. Sand, D.Sc.; and G. Martin, Ph.D, B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences in October, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. Evening students, 10s. for 2 hours per week, 3 hours 15s., 4 hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, free from the Registrar.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturers and Demonstrators—W. E. S. Turner, M.Sc., B.Sc.; W. J. Jarrard, B.Sc.; C. R. Young, B.Sc.; J. Kenner, Ph.D., B.Sc.

The Session will commence October 5th.

Matriculation Course. — Tuesday and Friday at 9 30. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, and Botany. And those for the Final Examination in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education.

Intermediate Course in Chemistry for B.Sc. or M.B., Ch.B.—Monday, Tuesday, Thursday, and Friday at 9 30 a.m. £5 5s., and six hours per week Laboratory work during first year.

B Sc. Course in Chemistry.—Monday at 9 30 a.m. and 12.30 p.m. during second year; Wednesday at 11.30 a.m., and Thursday at 10.30 a.m. and 12 30 p.m., during third year, £4 4s.; and nine hours per week Laboratory work during second and third years.

B.Sc. with Honours.—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for he degree. The third year is devoted to the advanced stutdy of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.

M.Sc.—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon any Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.

D.Sc.—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five year's standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory for one term are charged one-half, and for two terms two-thirds of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health is held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Board of Education, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full informa-

tion may be obtained on application to the Registrar of the University.

Evening Classes.—Lecture Class and Laboratory, on Thursday evening during the Michaelmas and Lent terms. Fee, £1 10s.

Department of Metallurgy.

Professor—J. O. Arnold, D.Met.

Assistant Professor—A. McWilliam, M.Met.A.R.S.M.

This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected. but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A new steel works has recently been erected in connection with the Sheffield University at a cost of about £15,000. The works include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works is also provided with a hammer capable of dealing with four-inch ingots Differential annealing furnaces and gas and electric hardening furnaces constitute part of the new plant. Additional laboratory accommodation is attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

The most recent addition to the steel works plant is a 3 cwt. Kjellin induction furnace worked by a 120 H.P. Motor-generator set with two-phase current. The Metallurgical Department of Sheffield University is (subject to an order by the King in Council) "in association" with the Royal School of Mines for teaching the advanced metallurgy of Iron and Steel.

UNIVERSITY COLLEGE, DUNDEE.

University of St. Andrews.

Professor of Chemistry—Hugh Marshall, D.Sc., F.R.S.

Assistant Lecturers—J. K. Wood, D.Sc. and (Vacant).

Lecture Assistant and Lab. Steward—J. Foggie, F.C.S.

The Winter Session begins early in October and ends in March. The Summer Session extends from the middle of April to the end of June.

The Junior Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

Chemistry.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators—Francis W. Gray, M.A., D.Sc., and Joseph Knox, D.Sc.

I. *General Lecture Course* (100 *Lectures*).— Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. *Physical Chemistry* (60 *Lectures*) —Three Lectures a week on Physical Chemistry are delivered during the Winter Session by the Lecturer, Dr. F. W. Gray. Fee, £2 2s.

III. *Inorganic Chemistry* (40 *Lectures*).—Two Lectures a week on Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Dr. J. Knox. Fee, £2 2s.

IV. *Special Lecture Course on Organic Chemistry* (50 *Lectures*).—Daily during the Summer Session. Fee, £3 3s.

V. *Practical Course for Medical Students.*—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

VI. *Chemical Laboratory.*—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. The Course qualifies for the examinations of the Institute of Chemistry. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

University of Aberdeen and Aberdeen and North of Scotland College of Agriculture.

Agricultural Chemistry.

Lecturer—James Hendrick, B Sc., F.I.C.

Assistants—R. Glegg, B.Sc., F.I.C.; A. J. Findlay, M.A., B.Sc. (Agr.), N.D.A., N.D.D.

I. Preparatory Courses in General Chemistry and in Organic Chemistry are given for those who are unable to take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. *Agricultural Chemistry* (*General Course*).—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. *Laboratory.*—A Summer Course in Practical Che-

mistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor—James Walker, D.Sc., Ph.D., F.R.S.

Lecturers—L. Dobbin, Ph.D.; A. C. Cumming, D.Sc.; W. W. Taylor, M.A., D.Sc.; and J. E. Mackenzie, Ph.D., D.Sc.

The three working terms are each of ten weeks' duration, viz.:—Autumn term, October to December; Spring term, January to March; Summer term, May to July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical students is given. The class meets daily; fee, £4 4s. The First Course for Arts and Science students meets three times a week throughout the year; fee, £4 4s. The Second Course is given on Organic, Advanced Inorganic, and Physical Chemistry. The class meets three times a week throughout the year; fee, £4 4s. Tutorial Classes are held in connection with the First and Second Courses. All Arts and Science Classes are open to Women Students.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Physical, Organic, and Inorganic Chemistry.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.). The Elementary Laboratory course for Arts and Science students is held for four hours per week during the year. Fee, £4 4s. The advanced laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. Fees: Whole Day—Year, £16 16s.; one term, £6 6s. Half Day—Year, £8 8s.; one term £3 3s. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis, Physico-chemical Measurements, Agricultural Chemistry, and Assaying). Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic Chemistry, Organic Chemistry, and Physical Chemistry. Practical Examination:—Complex Qualitative Analysis; Preparations; Gravimetric and Volumetric Analysis; Testing of Organic Substances. Each candidate taking the higher standard will also be examined on Ultimate Organic Analysis; Gas Analysis; Assaying; and Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry *may be* required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—A. Archibald Boon, B.A., B.Sc.; Andrew F. King, F.I.C.; Wm. Maitland, D.Sc.; F. D. Miles, B.Sc.

The Session begins Oct. 5th, 1910.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electro-chemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

For Students who have been three and four years in the Chemistry Department, arrangements have been made for their spending from four to twelve months in the laboratories of the Corporation's Gas Works, with a view to the study of problems connected with the Combustion of Fuel, the Manufacture of Coal-gas and its By-products, &c.

A Laboratory, under the charge of Dr. Emil Westergaard, has been provided for the study of Technical Mycology, including Brewing, Distilling, Malting, Vinegar Making, Tanning, Preserving, Starch and Sugar Making, Bread Making, Butter and Cheese Manufacture, &c.

Matriculation Fee, 5s.; Composition Fees from £12 12s. to £15 15s. Full particulars are published in the Calendar of the College, which is issued early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A

Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D

Lecturer on Dyeing—A. B. Steven, B.Sc.

Lecturer on Metallurgy—A. Campion, F.I.C., F.C.S.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 28.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses

extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1910-1911 may be had from Mr. H. F. Stockdale, Secretary; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

United College of St. Salvator and St. Leonard.

Professor of Chemistry—James C. Irvine, Ph.D., D.Sc.

The Session begins on October 6th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about thirty-seven Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 10th and following days. Twenty-two of these Bursaries are restricted to Men, one is open to Men or Women, and fourteen are restricted to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree, and the M.B., Ch.B. Degrees.; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Exams. in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s, and for the Advanced Course £5 5s.

Original Research.

A special Research Department has been instituted by the University, the laboratories of which are open to students who give proof of their capacity of conducting original investigation. Graduates of other Universities who spend two years in the laboratory as Research Students are eligible for the D.Sc. degree of the University, and, as far as possible, special chemicals and apparatus are provided free of charge. Graduate workers can also qualify for the Berry 1851 Exhibition and Carnegie Research Scholarships.

Students may work either independently or in collaboration with the Professor, to whom all communications should be addressed.

QUEEN'S UNIVERSITY, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., &c.

Lecturer on Organic Chemistry—A. W. Stewart, D.Sc.

I.—*Chemistry.*—The lectures are delivered at 12 o'clock, on the first five days of each week, and terminate at the end of March The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £3 3s.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3 3s.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £3 3s. for one term, £5 5s. for two, or £7 7s. for three terms.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Post Graduate Scholarships in Chemistry alone awarded annually of £50, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150. tenable for two or under special conditions for three years.

UNIVERSITY COLLEGE, CORK.

A Constituent College of the National University of Ireland.

Professor—Augustus Edward Dixon, M.D.

Demonstrators—John Taylor, M.Sc.; James L. McKee, B.A., Ph.D.

The College Session will commence on October 4th, 1910, and end on June 30th, 1911. All classes are open to male and female students.

The following courses are provided:—

1. First Year Course for B.Sc.—General and Elementary Physical Chemistry, Inorganic Chemistry, Introductory Organic Chemistry, Practical Chemistry.

2. Second Year Course for B.Sc.—Advanced Inorganic Chemistry, Advanced Organic Chemistry, Practical Chemistry.

3. Third Year Course for B.Sc.—Physical Chemistry, Advanced Organic Chemistry, Practical Chemistry.

4. Courses in Systematic and in Practical Chemistry for students of Medicine proceeding to the Degrees of the University, or to the Examinations of the Medical Licensing Bodies of Dublin and of Edinburgh.

5. Courses in Systematic and in Practical Chemistry for Students of Engineering.

6. Laboratory Practical Course for the Diploma in Public Health.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c,, are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

NATIONAL UNIVERSITY OF IRELAND.
University College, Galway.

Professor—Alfred Senier, Ph.D., M.D., D.Sc., F.I.C., F.C.S., M.R.I.A.

Demonstrator—Robert Robison, B.Sc., Ph.D., F.I.C.

Research Assistant—Frederick G. Shepheard, B.Sc., A.R.C.Sc.

The Session commences in October and ends in June.

Chemistry is studied by work in the Laboratories, by attendance at Lectures, and by the use of the College Library.

Faculty of Science.—1. *First Year's Courses.*—Laboratory: Inorganic preparations, simple gravimetric quantitative and simple qualitative determinations. Lectures: A study of the chief non-metallic elements, their reactions and compounds, the molecular and atomic hypotheses, the leading metals, and an elementary consideration of the constitution and reactions of typical fatty and aromatic organic compounds. 2. *Second Year's Courses.*—Laboratory: Organic preparations, complex qualitative and quantitative inorganic determinations. Lectures: Advanced inorganic and organic chemistry. 3. *Third Year's Courses*—Laboratory: Qualitative and quantitative organic determinations, molecular weight determinations, gas analysis, thermo-electro and photo-chemical and other physical determinations. Lectures: General, physical, inorganic, and organic chemistry, a detailed study of special branches, and the historical development of chemistry.

Faculty of Medicine.—First Year's Courses.—Laboratory: Same as in Faculty of Science, but less detailed, and including the detection of the chief alkaloids, glucosides, and carbohydrates, and the chemical examination of urine. Lectures: Same as in Faculty of Science, first year.

Faculty of Engineering.—First Year's Courses.—Laboratory: Same as in Faculty of Engineering, but less detailed, and including a special study of metals, alloys, and other materials used in building construction, also determination of hardness in waters. Lectures: Same as in the Faculty of Science, first year.

The College offers a Scholarship in Chemistry for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in the Faculties of Science, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by six Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar and other College publications may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Dean of Faculty and Professor of Chemistry—W. N. Hartley, F.R.S., D.Sc.

Lecturer on Organic Chemistry—Alphonsus O'Farrelly, M.A.

Senior Assistant—J. Holms Pollok, D.Sc.

Junior Assistant—J. Ivon Graham, A.R.C.Sc.I., B.Sc.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships are of the value of £50 a year for three years, and, in addition, entitle the holder to free instruction during the full Associateship Course.

For further particulars apply to the Registrar.

PROFESSIONAL CHEMICAL QUALIFICATION
(F.I.C. and A.I.C.).

The Institute of Chemistry of Great Britain and Ireland.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, to elevate the profession of Chemistry by setting up a high standard of scientific and practical proficiency for persons desirous of becoming professional consulting and technological chemists, public analysts, and chemical advisers; by examining Candidates, and granting certificates of competency; and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University recognised by the Council, or under the direction of a Fellow of the Institute in an approved laboratory. *The Intermediate Examination in General Theoretical and Practical Chemistry.*—Candidates for admission to the Intermediate Examination (Fee, £5 5s.) are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Higher Physics; (ii.) Advanced Mathematics; (iii.) Mechanics and Chemical Engineering; (iv.) Metallurgy; (v.) Geology and Mineralogy; (vi.) Physiology; (vii.) Bacteriology; (viii.) Agriculture; (ix.) Elementary Botany; (x.) Elementary Biology; and (III.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' day courses in a recognised Institution as indicated above, and work systematically for two other years under a Fellow of the Institute in an approved laboratory. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also taken at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Honours Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. A Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is

eligible for admission to the Final Examination, but Candidates taking the food and drugs section must take a course in botany, and those taking biological chemistry a course in biology. *The Final Examination* (Fee, £5 5s.) *for the Associateship* (*A.I.C.*).—This comprises, in addition to a general knowledge of all branches of chemistry, a thorough knowledge of one branch —mineral chemistry; metallurgical chemistry; physical chemistry; organic chemistry; chemistry of food and drugs, fertilisers and feeding-stuffs, soils, and water (including a compulsory examination in therapeutics, pharmacology, and microscopy); or biological chemistry. All Candidates for the Final Examination are required to translate French and German technological literature, with the aid of dictionaries. *Fellowship* (*F.I.C*).—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of applied chemistry in a manner satisfactory to the Council. Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (gratis) from the Registrar, 30, Bloomsbury Square, London, W.C. Past Examination Papers, 6d.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

City and Guilds of London Institute for the Advancement of Technical Education.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds Central Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons training to become Technical Teachers; 2. Persons preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in the various special subjects. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

City of London College, White Street, Moorfields.—I. S. Scarf, F.I.C., F.C.S., and Assistants. Courses of Saturday and Evening Lectures and Laboratory Practice in Chemistry and Physics, open to Students of both sexes. Day Commercial School. Session commences Sept. 26th.

Battersea Polytechnic.—Principal, Mr. S. G. Rawson, D.Sc., F.I.C. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), F.I.C., and Assistants. Session opens Sept. 27. Complete courses of Instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in Technical Bacteriology, Paper Making and Testing, and Oils, Fats, Soap, and Candles, Chemical Engineering, Dyeing and Cleaning, Food and Drugs Analysis, and Pharmacy and Dispensing.

Borough Polytechnic Institute, 103, Borough Road, S.E.—Chemistry Department under the Direction of C. Dorée, M.A., D.Sc. Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry. Special Lectures and Laboratory Courses in Electro-chemistry and Electro-chemical Analysis. Special Course of Lectures on Chemistry and Technology of the Essential Oils, by C. T. Bennett, B.Sc., A.I.C. Special Lectures and Laboratory Courses on the Chemistry and Manufacture of Foodstuffs, by Edward Hinks, B.Sc., F.I.C., and Thomas Macara, F.I.C., F.C.S. Special Course on Analysis of Laundry Trade Materials. Session opens Monday, Sept. 26.

Birkbeck College, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. Alex. McKenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. The Session will commence on Wednesday, Sept. 28, when Professor Sadler will give the Opening Address, at 7.30 p.m. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, History, and various branches of Law. All the Courses are conducted by recognised teachers of the University and provide for the Examinations of the University of London. Last session 45 students took Degrees in Arts and Science, 20 with Honours. The Calendar supplies detailed information respecting the Courses of Study, Examinations, &c.

Northern Polytechnic Institute, Holloway Road, N.—Principal, R. S. Clay, D.Sc.; Head of the Chemical Department, W. H. Mills, M.A., Sc.D.; Assistants, W. H. Watson, B.Sc., A.R.C.S.; Miss A. M. Bain, M.A., B.Sc.; and F. W. Linch, B.Sc., A.I.C. Instruction in theoretical and practical Inorganic and Organic Chemistry. Systematic Day and Evening Courses for the London University Degrees, Pass and Honours, also for the Board of Education examinations. The Session begins Sept. 19. Prospectus sent free on application to the Secretary.

Northampton Polytechnic Institute, St. John Street Road, E.C.—Principal, R. Mullineux Walmsley, D.Sc, &c.; Technical Chemistry, Mr. S. Field, A.R.C.S.; Mr. A. H. Munday, F.C.S.; and Mr. G. Naylor. Day and Evening Classes in Electro-chemistry, Electroplating, Electro-metallurgy, Electrotyping, Stereotyping, and Metal Colouring. (For full details see Prospectus).

South Western Polytechnic, Chelsea, S.W.—Principal, Sidney Skinner, M.A. Head of the Chemical

Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, Photography, &c. Systematic Courses are held for the Matriculation, Inter. Sci., and B.Sc. Examinations (Pass and Honours) of the University of London. The Day Course in Chemistry is of three years' duration; it gives a thorough training to those who wish to become Consulting or Industrial Chemists. Prospectus of Day and Evening Classes may be obtained from the Secretary, 1d., by post 4d.

East London College, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D. Lectures and Practical Classes are conducted in the Day Technical College, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination, B.Sc. (Honours and Pass). Special attention is given to work for the Honours Examination and research. Evening Classes for London University Degrees are also held.

University Tutorial College, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

Sir John Cass Technical Institute, Jewry Street, Aldgate.—Principal, Charles A. Keane, D.Sc., Ph.D., &c., assisted by H. Burrows, Ph.D., F.I.C., Arthur R. Ling, F.I.C., A. R. Smith, M.Sc., F.C.S., C. O. Bannister, A.R.S.M., Arthur Harden, D.Sc., J. S. S. Brame, and Wesley J. Lambert. The Session of the Sir John Cass Technical Institute will commence on Monday, September 26th. The Institute, which was founded by the Governors of Sir John Cass's Foundation, is specially devoted to technical training in experimental Science and in the Artistic Crafts. Graded curricula of study, extending over several years, are provided in the several departments of work, and in addition a number of special courses of instruction given by experts, so that there are full educational facilities in the subjects taught, both for youths and for those who have had no previous systematic training, and also for those holding responsible positions who desire to keep in touch with modern developments of the applications of science to industry. Amongst the special features of the syllabus for the new Session are courses of instruction on "Liquid, Gaseous, and Solid Fuel," arranged to meet the requirements of those engaged in chemical and engineering works or who are concerned with the use of fuel as a motive power; on the Fermentation Industries, including a special course on the Microbiology of the subject; on the various branches of Metallurgy, and on Scientific and Technical German. The aim of this last course is to provide for those engaged both in Pure and in Applied Science with an opportunity of acquiring a knowledge of scientific and technical terms employed in German with the view of enabling them to read German scientific and technical works and literature. Full details may be obtained on application, or by letter to the Principal.

East Ham Technical College.—Principal, W. H. Barker, B.Sc. Chemistry, A. E. Dunstan, B.Sc. Evening Classes and Secondary School.

Blackburn Municipal Technical School.—Chemistry: Mr. Robert H. Pickard, D.Sc.(Lond.)., &c., assisted by Messrs. Jos. Yates, M.Sc., F.I.C., W. O. Littlebury, B.Sc., F.I.C., Jos. Kenyon, B.Sc., A.I.C., and W. A. Jowitt. Session opens Monday, Sept. 19. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d.).

Leeds: Central Technical School, Leeds Institute, Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in all subjects of Science and Technology, among which are:—Chemistry (Inorganic and Organic), Chemical Calculations and Principles of Analysis, by Mr. R E. Barnett, B.Sc., A.R.C.S., Mr. J. B. Murray, Mr. A. McFarlane, and Mr. O. F. Kirby, M.A., B.Sc.; Metallurgy (Theoretical and Practical) and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Gas Manufacture, by Mr. W. E. Pettigrew; Oils and Fats, by Mr. W. Dillon; Magnetism and Electricity, Practical Physics, &c., by Mr. J. E. Tindall, B.A., B.Sc.; Bread-making and Flour Confectionery, by Messrs. W. H. Quinn and J. C. Hesselgrave; Photography, by Mr. S. E. Bottomley. Fees: from 7s. 6d. per session. Group courses arranged for Students engaged in Chemical Industries. Special three evening Course for Pharmaceutical Students, covering the "Minor" syllabus in three years, by Messrs. J. H. Gough, Ph.C., F.C.S.; S. Parrish, B.Sc., A.R.C.S.; and N. Walker. Session commences Sept. 19th. See the Technical Handbook, 2d. (by post 5d.). Prospectuses of various Classes free on application to the Head Master, or to Mr. James Graham, Secretary for Education, Calverley Street, Leeds.

Redruth School of Mines (now incorporated in the School of Metalliferous Mining, Cornwall).—Complete courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application.

Municipal School of Technology, Sackville Street, Manchester.—Laboratories and workshops for Mechanical, Electrical, Sanitary and Hydraulic Engineering, Textile industries, Photography, Collotype and Photo-mechanical processes, Letterpress and Lithographic industries, and industries within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity. The School is now established as the Faculty of Technology in the University of Manchester, and students of the School fulfilling the conditions can proceed to the Degrees of Bachelor and Master of Technical Science B.Sc. and M.Sc. Tech.). The Session commences Sept. 19.

Wolverhampton Municipal Science and Technical School.—Principal, J W. Coates, D.Sc.; Inorganic and Organic Chemistry, Mr. W. Whitehouse, F.C.S.; Physics, Messrs. W. Whitehouse and A. T. Harrison, B.Sc.; Botany, Mr. Sidney Phillips, Ph.C. Day Classes in Chemistry, and Evening Classes in Chemistry, Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students. Session commenced Monday, Sept. 12th. For other particulars and programme, apply Mr. G. F. Chell, Secretary.

Municipal Technical Institute, Belfast.—Principal, F. C. Forth, A.R.C.Sc.I. Chemistry, Prof. J. Hawthorne, B.A., Ph.D., and Assistants. Day and Evening Courses. Session opened Sept. 12th.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cli., No. 1, July 4, 1910.

Nature of the so-called Black Phosphorus.—D. Gernez.—Fused phosphorus dissolves mercury, giving a colourless solution, which remains colourless when the temperature is lowered, even if it is saturated or supersaturated with mercury. When the phosphorus solidifies, however, it separates from the mercury and turns black. The mercury is then finely divided in the mass; if the phosphorus is again liquefied the mercury dissolves and the whole becomes colourless.

Action of Iron and its Oxides on Carbon Monoxide at a Red-heat.—Armand Gautier and P. Clausmann.—At a red-heat carbon monoxide reacts with iron, giving carbon, carbides of iron, and carbon dioxide. If the iron is mixed with its oxides at an incipient red-heat, besides carbon dioxide and free carbon several carbides are obtained, including $Fe_{12}C$ (1·77 per cent of carbon) and Fe_5C (4·11 per cent of carbon); the former of these is more easily attacked by dilute sulphuric acid than the latter. Ferrous and ferroso-ferric oxides are also formed, and a small quantity of a substance which is soluble in hot caustic potash, and which the authors intend to identify. Dilute acids dissolve the carbides, giving methane and hydrogen, and at the same time there are indications of the formation of cyclic hydrocarbons. The carbides are decomposed by water-vapour even below 500°, and methane is formed in uantities which increase as the temperature is raised.

Constituents of the Induced Activity of Actinium.—L. Blanquies.—Bragg's curves obtained with polonium and radium C are superposable, while the induced activity of actinium gives a curve of different form. This difference could be explained by supposing that the induced activity of actinium contains a new substance of very short life which gives rise to AcB. The author has endeavoured to verify this supposition of the existence of a product AcB'. The results obtained are not conclusive, but at the same time they do not disprove the hypothesis.

Sodium Manganate and its Hydrates.—V. Auger.—Sodium manganate can be prepared very easily by decomposing the corresponding permanganate by means of soda. The salt yields hexa-, tetra, and decahydrates. Its chemical properties are the same as those of potassium manganate, except as regards the decomposition of the salts in presence of their alkaline base in excess; the sodium salt gives the mangani-manganate, $Mn_2O_5.3Na_2O.nH_2O$, and the potassium salt the salt $Mn_5O_{13}.5K_2O$. The chromate and manganate of sodium are isomorphous.

Decomposition of Thorium Sulphate by means of Water.—M. Barre.—The decomposition of thorium sulphate by water begins at 55°. A hydrate, $Th(SO_4)_2ThO_2.6H_2O$, is formed, but it is very unstable and is rapidly transformed into a basic salt containing four molecules of water.

Adsorption of certain Dyes.—Léo Vignon.—Some dyes, such as picric acid, are diffusible, but are not adsorbed; others (orange II., malachite green, &c.) are both diffused and adsorbed, while a third group (congo red, diamine green, &c.) are neither diffused nor adsorbed. There is no constant relation between diffusion and adsorption. The dyes of the second group are in colloidal solution after adsorption, while those of the first group are really dissolved.

Acetylenic Ketones.—E. André.—A good yield of ketones of general formula $R{-}C{\equiv}C{-}CO{-}R'$ can be obtained by allowing the acid bromide to act on the sodium acetylenic carbides in anhydrous ether. The oxidation of the secondary alcohols, $R{-}C{\equiv}C{-}CHOH{-}R'$, also gives fairly satisfactory results.

Isomaltol.—A. Backe.—The joint action of an enzyme and heat upon starch gives a substance (isomaltol) analogous to, but not identical with, maltol. Its formula is $C_6H_6O_3$, and from its behaviour on hydrolysis and oxidation its constitution appears to be expressed by the structural formula

$$CH_3{-}C(=CH{-}O{-}CH){-}CO{-}C(=CH){-}OH$$

Isomaltol is formed by the acid distillation of a substance which is produced in the same conditions as maltol. By distilling one kilogrm. of powdered biscuit 0·07 grm. of isomaltol can be obtained. Maltol and isomaltol can easily be separated by sublimation, the latter being volatile at the ordinary temperature.

New Method of Determining Glycerin in Wines.—C. Béys.—The wine is neutralised with baryta, evaporated to a syrupy consistency, sand is added, and the glycerin is extracted with acetone. The glycerin thus obtained contains a small quantity of foreign matter. This method has been found to give very satisfactory results.

Glucoside in Leaves of Pear Tree.—Em. Bourquelot and A. Fichtenholz.—By Bourquelot's method a glucoside can be extracted from pear leaves. This glucoside is hydrolysed by emulsin, and from its physical properties it appears to be identical with arbutin.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following were the Officers and Committee of Section B (Chemistry) at the Sheffield Meeting of the British Association:—

President—J. E. Stead, F.R.S., F.I.C., F.C.S.

Vice-Presidents—Prof. H. E. Armstrong, Ph.D., LL.D., F.R.S.; Prof. J. O. Arnold, D.Met.; Prof. W. P. Wynne, D.Sc., F.R.S.; Prof. H. M. Howe, LL.D.; Prof. Orme Masson, F.R.S.

Secretaries—E. F. Armstrong, D.Sc., Ph.D. (Recorder); F. M. Perkin, Ph.D.; T. M. Lowry, D.Sc.; W. E. S. Turner, M.Sc.

Committee—W. Barlow, F.R.S.; Prof. W. A. Bone, F.R.S.; Dr. G. T. Beilby, F.R.S.; Dr. S. M. Copeman, F.R.S.; Prof. E. Divers, F.R.S.; Prof. H. B. Dixon, F.R.S.; Dr. J. V. Eyre; T. Fairley; Dr. J. N. Friend; A. D. Hall, F.R.S.; C. T. Heycock, F.R.S.; Dr. A. Holt; H. O. Jones; Prof. McWilliam; Prof. H. A. Miers, F.R.S.; Prof. Parker; Prof. W. J. Pope, F.R.S.; H. Ramage; Sir Wm. Ramsay, F.R.S., K.C.B.; Dr. W. Rosenhain; Dr. H. J. Sand; Dr. I. Smedley; Miss Thomas; Dr. J. F. Thorpe, F.R.S.; Dr. G. Young; Prof. T. Turner; F. P. Worley.

The Papers brought before the Section were as follows:—

Mr. J. E. Stead—Presidential Address.
Prof. W. A. Bone—Report on Combustion.
Sir William Ramsay and R. W. Gray—The Molecular Weight of Radium Emanation.
Dr. J. A. Crowther—The Number of Electrons in the Atom.
Dr. R. D. Kleeman—The Attraction Constants of Molecules and their Chemical Properties.
Dr. J. V. Eyre—Report on Solubility.
F. P. Worley—The Deduction of Hydration Values of Acids from the Rate at which they induce Hydrolysis.
Prof. C. Féry—Autocollimating and Focussing Prism and a Simple Form of Spectrograph.
Dr. T. M. Lowry—Origin of Colour.
W. E. S. Turner and E. W. Merry—The Molecular Complexity of Nitrosoamines.

W. E. S. TURNER and C. J. PEDDIE—Molecular Association in Aqueous Solution illustrated by Hydroxyl containing Substances.
W. E. S. TURNER—The Problem of Molecular Association. I.—The Molecular Complexity of the Halogen containing Substances.
Dr. J. F. THORPE—An Instance illustrating the Relative Instabilities of the Trimethylene Ring as compared with the Tetramethylene Ring.
A. D. MITCHELL and Dr. J. F. THORPE—The Elimination of a Carboxethyl Group during the Closing of the Five Membered Ring.
Dr. J. KENNER and E. WITHAM—Formations of Tolane Derivatives from Benzotrichlorides.
Dr. J. KENNER and Prof. W. P. WYNNE—The Nitro, Chloro, and the Dichlorotoluene Sulphonic Acids.
Sir J. DEWAR and H. O. JONES—Gaseous Carbon Monosulphide.
Dr. F. M. PERKIN—The Action of Metals upon Alcohols.
Reports of Committees—
Hydroaromatic Substances.
Aromatic Nitroamines.
Isomorphous Benzene Derivatives.
Dynamic Isomerism.
Dr. F. F. BLACKMAN—The Biochemistry of Respiration. (Discussion).
R. BLAIR and Sir W. TILDEN—The Neglect of Science by Industry and Commerce. (Discussion).
Prof. ARNOLD—On a Fourth Recalescence in Steel.
Prof. H. M. HOWE—(*a*) Allotropy or Transmutation. (*b*) The Closing and Welding of Blowholes in Steel Ingots.
Prof. H. E. ARMSTRONG—The Provident Use of Coal.
Prof. A. McWILLIAM—Influence of Chemical Composition and Thermal Treatment on the Properties of Steels.
Dr. S. MONCKTON COPEMAN—Ferro-silicon: The Causation of Danger Incidental to its Transport and Storage. (Discussed by H. WILSON HAKE and S. R. BENNETT).
Dr. J. N. FRIEND—The Corrosion of Iron and Steel.
C. CHAPPELL and F. HODSON—The Corrosion of Iron and Steel.
Dr. W. ROSENHAIN—The Crystalline Structure of Iron at High Temperatures.
Report of the Committee on Electroanalysis.

Prof. Sir William Ramsay, K.C.B., F.R.S., has been elected President of the Association for the year 1911-12. The Meeting will be held in Portsmouth from August 30th to September 6th, 1911.

The Chemical Laboratory Fresenius at Wiesbaden.—During the Summer Term, 1910, fifty-two students, including ten ladies, attended the Chemical Laboratory Fresenius. Of these thirty-nine were from Germany, three from France, three from Russia, two from the United States of America, and one each from England, Holland, Roumania, Sweden, and Turkey. There were two assistants in the Teaching Laboratory and twenty-seven in the Private Laboratories (Versuchsstationen). To the certified staff of teachers belong the Directors, Geh. Regierungsrat Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Dr. L. Grünhut, Dr. R. Fresenius, and J. Huber (Architect). The next Winter Term begins on October 17th. During the Summer Term, 1910, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen), in the interests of trade, industry, mining, agriculture, hygiene, justice, and government.

Condensation of Phenolisoxazolone with Mesoxalic Ether.—André Meyer.—When phenylisoxazolone condenses with mesoxalic ether the colourless crystalline compound obtained has the formula $C_{25}H_{22}O_8N_2$, and is the mesoxalate of ethyl-bisphenylisoxazolone. It yields well-defined metallic salts, and from it the author has also prepared the diethyl, diacetyl, and dibenzoyl derivatives.—*Comptes Rendus*, cl., No. 26.

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THE CHEMICAL NEWS.

Vol. CII., No. 2652.

BRITISH ASSOCIATION.
HONOURS CONFERRED UPON SCIENTIFIC MEN AT SHEFFIELD UNIVERSITY.

The most brilliant gathering in the history of the University of Sheffield was witnessed in Firth Hall on Tuesday, the 6th, when a Degree Congregation was held in honour of the visit of the British Association to the City of Steel. Sitting on the throne in the centre of a raised dais was the Chancellor of the University (the Duke of Norfolk), robed in black velvet and golden braid. Earl Fitzwilliam in scarlet robe was seated immediately to his right, and next him the Rev. Prof. Bonney. To the left were seated the Pro-Chancellors (Mr. George Franklin and Mr. H. K. Stephenson).

All eyes, however, were concentrated on the group of savants, robed in brilliantly coloured doctor's robes, who sat in the body of the hall near the throne waiting to be called to occupy posts of honour left vacant for them on the front of the dais.

The Public Orator (Prof. Appleton) stepped forward to the front of the throne as each recipient of honour in rotation advanced to the throne and raised his hat in compliment. Then, facing the Chancellor, he delivered a well-thought-out oration which might have done credit to a Demosthenes, so that the world might know whom Sheffield sought to honour.

Degrees were conferred as follows :—

Doctor of Science—

Thomas George Bonney, F.R.S.
William Bateson, F.R.S.
Sir William Crookes, O.M., F.R.S.
Francis Darwin, F.R.S.
Thomas William Rhys David, F.R.S.
Sir Archibald Geikie, Pres.R.S.
Ernest William Hobson, F.R.S.
Sir Joseph Norman Lockyer, F.R.S.
Sir Oliver Joseph Lodge, F.R.S.
Henry Alexander Miers, F.R.S.
Sir William Ramsay, F.R.S.
Charles Scott Sherrington, F.R.S.
Sir Joseph John Thomson, F.R.S.

Doctor of Engineering—

Sir Joseph Jonas (Sheffield).
Sir William Henry White, F.R.S.

Doctor of Metallurgy—

John Edward Stead, F.R.S.

Prof. Appleton, who presented the recipients of Degrees to the Chancellor, said :—

Dr. Bonney.

"The distinguished attainments of the Rev. Prof. Bonney are by this time almost as familiar to the ordinary citizen of Sheffield as they have long been to the members of that famous Association of which he is this year the President. It is in that capacity that this University to-day delights to honour him; at the same time she honours herself by placing on the roll of her honorary graduates the name of one who has long held rank among the leading geologists of the world. It is specially appropriate that the University which the late Dr. Sorby did so much to found should confer the highest distinction in its power upon a scientist who has so materially contributed to that study of microscopical petrology of which Dr. Sorby was the father. Not only has Dr. Bonney unravelled the structural secrets of some of the most difficult of the rocks of Britain, but he has devoted special attention to the crystalline schists of the Alps, and has traced the diamond to its home in the eclogite of South Africa. In less specialised fields he has investigated many problems of physical geology—the action of glaciers, the formation of lake basins, the nature and origin of volcanoes, and the conditions of the formation of triassic rocks; and in addition to all this mass of scientific work he has found time to write many volumes of a more literary character which have made his name familiar to many to whom pure science is a sealed book."

Mr. William Bateson

"May almost be called the founder of an entirely new school of Biological research. He was the first scientist to make a serious attempt to show the real bearing of the principle of discontinuity in variation upon the problem of evolution; and he was the first Englishman to recognise the true import of the almost forgotten theory of heredity that was put forward a generation ago by the Austrian monk Mendel. Mr. Bateson and his coadjutors have succeeded in accumulating a mass of experimental evidence of the truth of Mendel's law, and have thereby probably placed us on the threshold of a new epoch in our knowledge of organic evolution."

Sir William Crookes

"May be said to have devoted his whole life to scientific investigation purely and simply for investigation's sake. It is nearly fifty years ago that he discovered a new element, Thallium, and since then he has built up for himself a great reputation in many branches of chemistry and physics. His work in connection with high vacua and radiant matter was epoch-making in its importance, and his more recent work as a pioneer in the separation and determination of the rare earths is specially remarkable for the accuracy, the acuteness of observation, the dogged persistence and unwearying patience for which he has always been noted as an investigator."

Dr. Darwin

"Is the distinguished son of a world-famed father, one who has earned quite remarkable distinction both in the world of letters and in the world of science. His writings upon the life and letters of Charles Darwin display literary gifts of a high order, while in his botanical work he has not only developed certain lines of his father's work in connection with the study of the sensitiveness and movements of plants, but he has also, by means of new apparatus of the most ingenious and delicate kind, observed the process by which water is given off from the leaves of plants and the method by which such loss of water is controlled by plants."

Prof. Rhys Davids

"Is recognised at home and abroad as the greatest living authority upon Pali—the sacred language of Buddhism—and upon Buddhist literature generally. He is the founder and president of the Pali Text Society, for which he has edited several of the sixty-five volumes already published. Prof. Davids is the great authority also upon the history and general condition of India during the early centuries of Buddhism, and holds a very high place among the students of early religions generally."

Sir Archibald Geikie

"Stands in the very first rank of modern geologists—distinguished at once for the quantity and the diversity of his original research, for the great extent of his field experience, and also for the number and the excellence of the educational works by which he has so materially contributed to the advancement and the diffusion of geological knowledge. His works upon Scottish scenery, upon volcanoes and volcanic action, upon the old red sandstone have long been rated, each in its special line,

among the classics of geological literature; and his power of clothing the bare facts of science in the most fascinating literary garb has gained for him readers and students wherever the English language is spoken. In the most remarkable degree he has combined the function of an original investigator with that of a most attractive and persuasive teacher."

Prof. Hobson.

"The name of Prof. Hobson is familiar to all mathematicians. From his early work in the lowly regions of applied mathematics, he has more recently soared into the dizzy altitudes of the highest and purest mathematics—where few indeed can follow him. Transfinite numbers—numbers which transcend all finite ideas—are Prof. Hobson's playthings; and it is whispered that he has clear ideas of a series of numbers which transcend in magnitude all transfinite numbers to as infinite extent as the transfinite numbers transcend those of everyday life. He has great influence with the younger mathematicians of his own and of other universities, and played an important part in the remodelling of the mathematical tripos at Cambridge."

Sir Norman Lockyer.

"The reputation of Sir Norman Lockyer rests upon many and varied grounds. Among other results of a lifetime devoted to the study of solar physics he was one of the first to render possible the detection and observation of the solar prominence otherwise than at a time of total eclipse; by his prolonged study of the periodic changes in the sun's spectral lines he has made enormous additions to our knowledge of solar spectroscopy, and of late years he has turned his knowledge of the sun and the stars to help in the solution of some of the problems of archæology."

Sir Oliver Lodge.

"Sir Oliver Lodge bears a name familiar to all members of this congregation and to most of the world outside it. Among physicists his work on the relations between matter and ether has long been recognised as of outstanding value; and it is a well known fact that, working deliberately upon Maxwell's theory of electro-magnetic field, he obtained almost simultaneously with Prof. Hertz experimental evidence of what we now know to be the basis upon which the whole theory of wireless telegraphy rests. To the world at large Sir Oliver Lodge is noted for the breadth and diversity of his interests and the vitalising force of his personality. To the world of education, as the first principal of the University of Birmingham, he has shown what enthusiasm and determination can do to win popular recognition for the highest University learning in a modern industrial centre."

Dr. Miers.

"Dr. Miers is one of those who has contributed largely to the progress which has recently been made in our knowledge of crystallography—especially in his papers on the variation of angles observed in crystals and upon the spontaneous crystallisation of the substances which form a continuous series of mixed crystals. As Waynflete Professor of Mineralogy at Oxford, he did much towards the foundation of a mineralogical school at that University, and his "Introduction to the Scientific Study of Minerals" is likely to remain a classical authority on the subject to which he has devoted the greater part of his life."

Sir William Ramsay.

"Sir William Ramsay has long since proved himself a most brilliant and original investigator in connection with that important group of subjects which lies on the borderland between physics and chemistry. Since the world-famous researches into the properties of Argon, which he conducted in collaboration with Lord Rayleigh, he has had a series of scientific triumphs. He discovered many years ago the existence as a terrestrial substance of that new element, helium, which he has more recently proved to be one of the products of the disintegration of the mysterious substance, radium. By a series of the most delicate experiments he has also succeeded in isolating from the air a complete group of new elements, entirely devoid of chemical properties, and has achieved the unique distinction of adding, not one element merely, but an entire group of Mendeleeff's Periodic Table."

Prof. Sherrington.

"Prof. Sherrington is honoured among physiologists at home and abroad for the original work he has done especially in connection with the brain and the nervous system. He is a most indefatigable and penetrating student of the intricacies and function within that system, and has added very materially to our knowledge of all the structures and processes that are associated with the activities of the mind."

Sir Joseph Thomson.

"The name of Sir Joseph Thomson must take a very high place even in this distinguished company of scientists. Both in the region of pure theory and in that of experimental work he has long held an almost unique position; in both cases mainly in that interesting and important department of scientific knowledge which belongs partly to physics and partly to chemistry. His own work has thrown a flood of light, derived from many sources, upon the nature and the constitution of matter, and his laboratory has been and is the inspiration and the training ground of a host of young investigators, especially in those great fields of research that have been opened up by the study of the conduction of electricity through gases for which he has done so much."

Sir Joseph Jonas.

"Sir Joseph Jonas has long been a familiar figure in the civic and educational life of this city, and it would be difficult to over-estimate his services in either capacity. As Lord Mayor he took a leading part in the management of this University; as vice-chairman of the Committee of the Applied Science Department he has exercised a controlling influence over this most important branch of our educational system, and as acting chief of a firm which represents a leading Sheffield industry, he has exemplified in a most striking manner the results which may be attained by the association of pure science with industrial practice."

Sir William White.

"To the world of marine engineers the name of Sir William White is the name of names, and nowhere is it held in greater reverence than here in Sheffield. He may fairly be called the father of the modern fighting ship; he has done for the world's navies what Brunel did for its mercantile marine, and of such vital importance were the services he rendered to our navy during the years when he was responsible for the design of each of its units, that Parliament acknowledged them by special act and grant. The principles of naval architecture laid down by him have been adopted in every shipbuilding yard in the world, and his pupils have covered the great waters with the copies or the developments of his designs."

Mr. J. E. Stead.

"Mr. J. E. Stead is universally recognised as one of the leading authorities upon metallurgical subjects. He has contributed largely to the expansion of the science of metallography, and has probed deeply into the different problems which arise out of the study of the crystallisation of iron. His researches into the relationships between iron and phosphorus are amongst the acknowledged classics of the metallurgy of iron and steel. For the University of this City of Sheffield it is a peculiar pleasure to honour one so distinguished in connection with the science to which her own industries are so greatly indebted."

The President of the British Association (Prof. Bonney), responded at the close of the ceremony, thanked the Chancellor for the great honour conferred upon his colleagues and himself, and of which they were keenly sensible. He thanked the University for the leading part it had taken in welcoming the British Association to the city and for the admirable arrangements in which it had co-operated.

Sir Oliver Lodge, in replying, made reference to the absence from the congregation of the Vice-Chancellor (Sir Charles Elliot), who met with a motor accident just over a week ago, and expressed much regret on that account. Remarking that he was present at the last visit of the Association to Sheffield, in 1879, Sir Oliver said that the advancement and improvements in the city were very notable, especially to an outsider who, like himself, had not seen much of the place in the time which had since elapsed. He recalled that on that occasion Sir William Crookes, the veteran now happily with them, brought forward in a great lecture what was practically the discovery of the cathode rays, a discovery which underlay and was the precursor of radio-activity, and of the great progress which had been going on in late years, and which some of them more or less knew about. The pioneer work of the phenomena of vacuum-tubes we owed also to Sir William Crookes and the great lecture in Sheffield in 1879. There had since been an upward march, and the university laboratory had delivered up its secrets to pertinacious investigators, and now there was a time ahead—for which that University stood—of earnest spirit and open mind.

RELATION OF SPECTRA TO THE PERIODIC SERIES OF THE ELEMENTS.*

By Prof. W. M. HICKS.

The author described some results recently obtained by him in a critical study of the spectral series of the second and third groups of the Periodic Table of Elements, more especially their dependence on the atomic volume of the element. Formulæ constants obtained from the wave-numbers of three lines of the Sharp series are definite functions of atomic weight and atomic volume. The exact form of the function of atomic weight had not been yet determined, but when it is known the measurement of the wave-lengths of a spectrum should give one of the most accurate methods of determining the atomic weight of an element. The function of the atomic volume was so far determined as to give deductions of atomic volume, or of density, very close to observational values in the case of the first three groups of the Periodic series.

Applying the method to the spectrum of europium as given by Exner and Haschek, a density of 13·1 was predicted for that element.

AN INSTANCE ILLUSTRATING THE RELATIVE INSTABILITY OF THE TRIMETHYLENE RING AS COMPARED WITH THE TETRAMETHYLENE RING.†

By Dr. J. F. THORPE, F.R.S.,
Sorby Research Fellow in the University, Sheffield.

The instability of a ring of three carbon atoms, they said, is illustrated by the fact that certain compounds of this type behave as $\alpha\beta$-unsaturated ethyl salts, and readily form condensation products with substances of the type of ethyl malonate. The process of forming condensation products in this manner has been used for the formation of open chain nitriles, because it has been found that the nitriles produced in this manner readily pass into imino derivatives of cyclopentane. An attempt was therefore made to apply this reaction to the corresponding derivatives of the four carbon ring in order to find if the open chain nitrile produced in this manner would pass into the corresponding derivative of cyclohexane. It was found that the four carbon rings remain under the experimental conditions employed entirely unaffected, but that a condensation product isomeric with that desired was produced by the formation of an imino compound with the nitrile group of the ring. It was also found that derivatives of the trimethylene ring, having two carbethoxyl groups on different carbon atoms, also formed condensation products, but that the cis modifications of these ethyl salts appeared to enter into condensation much more readily than the isomeric trans modifications. These condensation products pass at once into derivatives of cyclopentane, but, owing to the fact that the open chain compounds have no more than one carbethoxyl group attached to any carbon atom ring, formation is effected without the production of ethyl carbonate.

THE ELIMINATION OF A CARBETHOXYL GROUP DURING THE CLOSING OF THE FIVE MEMBERED RING.*

By A. D. MITCHELL and Dr. J. F. THORPE, F.R.S.

It was shown that the closing of an open chain of five carbon atoms to form a five-membered ring imparts to the molecule a condition of tension which limits the capacity of the constituent carbon atoms of combining with groups of more than a certain volume. Thus the closing of the five ring to form the two hydrindones or their derivatives necessitates, in the first instance, the freeing of the carbon atoms constituting the rings from these groups of high molecular volume, otherwise the closing of the ring does not ensue. The actual instances dealt with in the present experiments were those derived from α-hydrindone, and it was shown that when the open chain nitrile, from which this substance can be derived, contains two carbethoxyl groups on the same carbon atom, one of these groups is quantitatively eliminated as ethyl carbonate before the closing of the ring. The carbethoxyl group is also eliminated in like manner if a nitrile group and a carbethoxyl group are attached to the same carbon atom of the open chain nitrile, whilst if an acetyl group and a carbethoxyl group are attached to one carbon atom the acetyl group is completely eliminated as ethyl acetate prior to the closing of the ring.

ALLOTROPY OR TRANSMUTATION?†

By Prof. HENRY M. HOWE, LL.D.

If after defining "elements" as substances hitherto indivisible, and different elements as those which differ in at least some one property, and after asserting that the elements cannot be transmuted into each other, we are confronted with the change from diamond into lampblack, and with the facts, first, that each is clearly indivisible hitherto and hence an element, and, second, that they differ in every property, we try to escape in a circle by saying that they are not different elements because they do change into each other. In short, we limit the name "element" to indivisible substances which cannot be transmuted into each other, and we define those which do transmute as *ipso facto* one element, and then we say

* Abstract of a Paper read before the British Association (Section A), Sheffield Meeting, 1910.
† Abstract of a Paper read before the British Association (Section B), Sheffield Meeting, 1910.

* Abstract of a Paper read before the British Association (Section B), Sheffield Meeting, 1910.
† A Paper read before the British Association (Section B), Sheffield Meeting, 1910.

that the elements cannot be transmuted. Is not this very like saying that, if you call a calf's tail a leg, then a calf has five legs? And if it is just to reply that calling a tail a leg does not make it a leg, is it not equally just to reply that calling two transmutable elements one element does not make them so?

Is it philosophical to point to the fact that two such transmutable elements yield but a single line of derivatives as proof that they are one element? Is not this rather proof of the readiness, indeed irresistibleness, of their transmutation? Does not this simply mean that the derivativeless element, whenever it enters into combination, inevitably transmutes into its mate which has derivatives?

We have become so accustomed to the present point of view that it seems to us second nature; but if we look frankly at it, is it a tenable or philosophical point of view?

This question is not without a practical application. If, instead of saying "The elements cannot be transmuted into each other," we were to say "Hitherto no elements have been transmuted into each other except those which transmute so readily that the derivatives of only one of them have been recognised," we should take a point of view from which the transmutation of, say, copper into lithium ceases to be so improbable antecedently as to call for extraordinarily conclusive evidence.

THE CLOSING AND WELDING OF BLOWHOLES IN STEEL INGOTS.*

By Prof. HENRY M. HOWE, LL.D.

In the solidification of molten or liquid substances, especially those of high melting-point, two classes of cavities are likely to form: gas bubbles called "blowholes," and a central contraction cavity called a "pipe."

The blowholes represent (*a*) the progressive concentration in the molten or liquid mother mass of the gases initially present, a concentration carried on to supersaturation, and to the liberation of part of this gas from the supersaturated layers; and perhaps (*b*) in some cases, such as that of the solidification of steel ingots, the formation of a gas from chemical reaction brought about by fall of temperature or by passage from the liquid to the solid state. In the case of steel ingots there are indications that carbonic oxide is thus formed during solidification by the union of carbon and oxygen present side by side in the molten metal.

The formation of the central "pipe" is due to the cooling, and hence contraction of the different layers of the mass æoliotachically, *i.e.*, at different rates *inter se*. In the first stages of solidification the outside of the mass, especially if it is cast in a cold iron mould, cools much faster than the still molten interior. The early excess of contraction of the outside, caused by this excess of cooling, is resisted by the lagging interior, with the result that the outer layers are virtually stretched beyond their normal dimensions, so that when solidification is complete the interior, which in the latter part of the cooling has to cool through a greater range of temperature and hence has to contract more than the outside, no longer suffices to fill that outside completely, and this deficit of volume of the interior is represented by a central cavity overlying the region in which the last of the solidification occurs. This same excess of contraction of the earth's crust in its early stages should later throw that crust into great compression, which may be an important element in volcanic and earthquake phenomena.

Blowholes themselves tend in effect to expand the volume of the interior as a whole without changing its outer dimensions and thus to lessen the deficit or pipe.

In case of steel ingots this pipe may reach very deep into the axis, and, because it is hard to work up, may compel us to disregard as much as one-third of the ingot in order to get sound unpiped metal. To avoid this some makers of steel of a composition favourable to welding have purposely allowed blowholes to form rather abundantly, so as to prevent the formation of a pipe, and, relying on the ease with which such steel welds, have tried to get flawless metal by welding these blowholes up in the process of rolling the ingot out into its final form, such as that of a boiler plate.

This procedure is of great economic importance, in that it enables the steel-maker to avoid the serious discarding which would be necessary in case his ingots were free from blowholes and hence deeply piped. But many intelligent metallurgists have condemned this practice on the ground that the closing of blowholes is impossible, because the gas which they contain must remain ever present during the rolling, even though somewhat compressed.

In some late investigations I have carried out two lines of inquiry as to whether the gas of the blowholes is qualitatively absorbable and whether the sides of the blowholes themselves are qualitatively weldable under the conditions of actual manufacture. Both lines proceed by comparing the metal in slabs cut from the original ingot without rolling, with metal cut from a boiler plate into which that same ingot was rolled, and cut in such a way as to separate and distinguish those parts of the metal in the plate which had originally been porous when in the ingot from those which had originally been compact.

The first line showed that the enormous differences in density which existed between the porous and the compact parts of the ingot were practically completely obliterated in rolling the metal down into a boiler plate. In one case the initial difference of 16 per cent in density was completely removed; in the other the initial difference of 10 per cent in density was reduced to one-fiftieth its original quantity.

This tended strongly to confirm the strong antecedent probability that the blowhole gases could be reabsorbed during the rolling process, thanks to its high temperature and pressure.

The second line of enquiry disclosed what traces of blowholes remained in the boiler plate by cutting very thin slices lengthwise and crosswise from that plate, mirror-polishing them, and then bending them double in such a way that any blowhole traces present ought to gape open like the cards of a bent pack. Had there been no welding of blowholes this bending should have disclosed unwelded seams about 3·5 inches long and 1·3 inches wide. In point of fact the traces detected were so short as to indicate strongly that a very great degree of welding had occurred. It had seemed to me extremely probable, antecedently, that such welding ought to occur; but here some very competent writers had differed with me. The longest single trace was 0·7 inch long. Only one important "string" of such traces was found, and this was only 0·3 inch long. Further, the scantiness of these relics of blowholes tends to show that the blowhole gases have been re-absorbed by the metal to a very great degree. I suggest that such relics of blowholes as have persisted represent in most cases spots where the re-absorption of the gas has become complete after the temperature has fallen too low to permit welding. I therefore suggest prolonging the exposure to a temperature above the welding-point, so as to complete the re-absorption of gas while the metal is still weldable.

The re-absorption of the blowhole gases and the welding of the blowholes ought to be promoted rather by the practice of "re-heating" than by that of "direct rolling." In the former the ingot is rolled part way towards its final shape, and the resultant "bloom" is then re-heated before further rolling; in the latter the ingot is rolled to its final shape, such as a rail or a boiler plate, at a single heat. During the early part of the rolling the metal surrounding each blowhole should become strongly charged with gas

* A Paper read before the British Association (Section B) Sheffield Meeting, 1910.

re-absorbed from that blowhole because of the enormous pressure caused by rolling. To re-heat the bloom exposes it for a long time to a high temperature in the heating furnace, during which time the gas dissolved in the neighbourhood of the blowhole has an opportunity to diffuse away, and the gas in the blowhole has a chance to be re-absorbed by the adjacent metal. And, further, the high temperature of the rolling immediately after this re-heating facilitates both the further absorption and outward diffusion of whatever gas remains in the blowholes and the welding up of their sides.

THE FIXATION OF NITROGEN BY FREE LIVING SOIL BACTERIA.*

By Prof. W. B. BOTTOMLEY, M.A.

Since the discovery of the Azotobacter group of nitrogen-fixing organisms by Beijerinck in 1901 numerous attempts have been made, but with little success, to utilise these organisms for increasing the store of soil nitrogen. Gerlach and Vogel (1902) and Freudenreich (1903) obtained negative results in soil experiments. Lipman (1904), experimenting with *Az. Beijerincki* and *Az. Vinelandii*, found that out of ten experiments there was a *loss* of nitrogen in every case but one, and this showed a gain of only 4 mgrms.

Certain results from inoculation experiments on clover with oats in 1907, and the discovery that species of Azotobacter and Pseudomonas are always found in association in the algal zone of the root-tubercles of Cycas, suggested that a mixed culture of these organisms might be effective in fixing nitrogen in the soil.

Pure cultures of the organisms obtained from Cycas root-tubercles incubated for fifteen days at 24° C. gave the following :—

	Mgrms. N per unit carbohydrate per 100 cc.
Control	0·48
Azotobacter	0·56
Pseudomonas	0·91
Azotobacter + pseudomonas ..	1·24

Hence Azotobacter and Pseudomonas fix more nitrogen per unit of carbohydrate when grown together than when grown separately. Further investigation showed that this increased fixation applied also to Azotobacter and Pseudomonas from ordinary soil and leguminous nodules respectively. Pure cultures grown in a solution consisting of mannite, 0·5 grm.; maltose, 0·5 grm.; potassium phosphate, 0·1 grm.; magnesium sulphate, 0·02 grm. per 100 cc. of water, at 24° C. for ten days, gave the following averages :—

	Mgrms. N per 100 cc.
Control	0·53
Azotobacter	2·19
Pseudomonas	2·30
Azotobacter + Pseudomonas ..	4·51

Owing to the different cultural conditions prevailing in soil and culture solutions an attempt was made to acclimatise the pure cultures to ordinary soil conditions. About 14 pounds of autoclaved garden soil was well moistened with the mixed culture and incubated for twenty-one days at 24° C. A culture solution was then obtained by mixing 5 grms. of this inoculated soil in 100 cc. of water with 1 grm. of sugar and incubating for twenty-four hours only; 50 cc. of this solution was then applied to pots containing 5 ounces of soil each, and incubated at 24° C. for ten days. The nitrogen determinations yielded :—

	Mgrms. N per 100 grms.
Soil + 50 cc. distilled water	324
Soil + 50 cc. autoclaved culture ..	330
Soil + 50 cc. living culture	359

An increase of 35 mgrms. nitrogen per 100 grms. of soil, which represents an increase of about 350 pounds of nitrogen per acre, taking an acre of soil 4 inches deep as weighing 1,000,000 lbs.

To further test the effect of the mixed culture (both pure culture and soil culture) under ordinary conditions on different soils, a number of shallow plant-dishes, each containing 3 pounds of soil and inoculated with 300 cc. of the culture, were kept in one of the greenhouses at the Chelsea Physic Gardens for fourteen days. Analyses of these gave the following averages :—

	Soil A.	Soil B.	Soil C.	Soil D.
	Mgrms. N per 100 grms. soil.			
Control	371	375	312	402
Pure culture ..	403	396	336	421
Soil culture ..	406	395	333	424
	Increase.			
Pure culture ..	32	21	24	19
Soil culture ..	35	20	21	22

Experiments in progress indicate that this fixed nitrogen is readily assimilated by plants, and crops are benefited by an application of the mixed culture.

* A Paper read before the British Association (Subsection B), Sheffield Meeting, 1910.

NOTES ON THE NATURE OF NITROGEN FIXATION IN THE ROOT NODULES OF LEGUMINOUS PLANTS.*

By JOHN GOLDING, F.I.C.

Nearly a quarter of a century has elapsed since Hellriegel and Willfarth showed that leguminous plants are able to assimilate the free nitrogen of the atmosphere when nodules are developed on their roots; but the problem of what takes place in the root nodule is still unsolved.

Numerous researches have led to the following conclusions :—

1. That the plant is able to get all its nitrogen from the air of the soil, and that the quantity fixed is very large.

2. That the nodule is the seat of the process.

3. That fixation is accompanied with a change in the form of the organism, which invades the root hair as an infection thread, passes through a rod-shaped stage, and finally assumes the (Y) bacteroid form.

4. That practically each plant has its own nodule organism, and though the differences seldom amount to a difference of species, it takes a considerable time for the nodule organism of one plant to become adapted to another plant, and when so adapted it is not capable of infecting the plant from which it was first taken.

5. That this adaptation to a particular kind of plant is retained by the organism in the soil for a considerable period, during which assimilation, if it takes place at all, is much less than when the organism is in the nodule.

The conditions which obtain in the nodule are as follows :—

The acidity of the cell sap must be contended with. Nitrogenous products of growth must be removed at an early stage of development of the plant. The organism must be fed with some carbohydrate, to give it the necessary energy to fix the nitrogen. Some limiting factor must restrict the number and size of the nodules. Chemical differences must exist between the roots of nearly related plants to which the organisms must be very sensitive. The atmospheric conditions obtaining in the nodule may also differ from those in artificial cultures.

The study of the behaviour of these organisms under controlled conditions of artificial culture, approximating as far as possible to the natural conditions, indicates a solution of the problem in the near future.

* A Paper read before the British Association (Subsectian B), Sheffield Meeting, 1910.

In some work on the subject quantitative determinations of the nitrogen fixed have been the measure of advance, while in others the formation of bacteroids, or of slime, or even the power of infecting plants, has been taken to indicate an approach to natural conditions.

A new method described and demonstrated for the first time indicates that it is the reaction of the medium which plays an important *rôle* in nitrogen-fixation. The cultures also disclose previously unobserved properties of the nodule organism.

Previous work is summarised, indicating that it is not only the acidity of the root sap, but also the removal of the products of growth, the supply of carbohydrate, and the slime production which must be regulated before artificial cultures of the organism can be expected to fix nitrogen to an extent comparable with that which takes place in the nodule. The ready adaptation of the organism to its environment must also be borne in mind.

ELECTRO-ANALYSIS.*

The work on electro-analysis has been further elaborated during the year by the publication of papers on the "Electro deposition of Metals," by Dr. F. Mollwo Perkin and W. E. Hughes (*Trans. Faraday Soc.*, 1910, vi.), and by Dr. H. J. S. Sand on "Apparatus for the Rapid Electro-analytical Separation of Metals (*Ibid.*, 1909, v., 159), and "The Electro-determination of Lead as Peroxide" (*Ibid.*, 1910, v., 207).

Perkin and Hughes have devised and experimented with new cathodes for the rapid deposition of metals. One simple smooth cathode is in the form of an elongated thimble, and with this, when rapidly rotated, very smooth and even deposits can be obtained; the total active electrode surface is about 16·3 sq. cm. Extended work has shown, however, that a platinum gauze cathode surrounding a spiral anode, which is rapidly rotated, gives the most satisfactory results. For separation of metals by means of graded potentials a funnel-shaped vessel with a tap for running off the electrolyte is used. This vessel has a side-tube fused into it at about the centre to take the capillary of the auxiliary electrode. This form of apparatus gave very good results, and is very simple in working.

The experiments referred to a year ago by Dr. Sand with an anode made partly of glass and a cathode of metals, other than platinum, have been completed by him, and will be published shortly. Satisfactory results for copper were obtained with a cathode of silver, and for zinc with a cathode of nickel. In the former case the electrolyte deposit may be removed from the electrode by a solution of hydrogen peroxide in diluted sulphuric acid.

Experiments on the separation of the four metals—copper, antimony, tin, and lead—have been continued. In connection with this work it has been shown that chlorides exert a retarding influence on the deposition of copper. This is due to the formation of derivatives of cuprous chloride during electrolysis from which copper is only deposited at a high potential. The conditions for the separation of copper from antimony have been fully elaborated, and mixtures of the three metals—copper, antimony, and tin—corresponding to industrial alloys have been successfully analysed. When lead is present in small quantity this may be deposited with the tin; the greater part of the tin may afterwards be removed by making the electrode the anode in a solution containing sodium polysulphides. The lead may then be separated from the small quantity of remaining tin by means of nitric acid, and can afterwards be deposited electrolytically (Preliminary Note in *Proc. Chem. Soc.*, 1909 xxv., 228).

* Report of the Committee, consisting of Professor F. S. Kipping (Chairman), Dr. F. M. Perkin (Secretary), Dr. G. T. Beilby, Dr. T. M. Lowry, Professor W. J. Pope, and Dr. H. J. S. Sand. Read before the British Association (Section B), Sheffield Meeting, 1910.

DYNAMIC ISOMERISM.*

Absorption-spectra of Camphor and its Derivatives.

The study of a large number of derivatives of camphor (*Trans. Chem. Soc.*, 1909, xcv., 807—823, 1340—1346; 1910, xcvii., 899—905, 905—921), has shown that a band is normally present at a frequency 1/3500, but penetrating only to log. thickness 2·6 (about 400 mm. of N/1000 or 40 mm. of N/100 solution). This band appears even when the two hydrogen-atoms of the adjacent methylene group are displaced, provided that the new radicles do not possess any large residual affinity; but in compounds such as $\alpha\alpha'$-dibromocamphor, $C_8H_{14}\begin{cases}CBr_2\\|\\CO\end{cases}$, and $\alpha\alpha'$-chloronitrocamphor, $C_8H_{14}\begin{cases}CCl.NO_2\\|\\CO\end{cases}$, the general absorption is increased by the substituent groups, and the band disappears. The development of the band can only be attributed to the carbonyl-group, which is therefore capable of giving rise to a specific or local absorption; this is only of slight intensity, and of such a frequency as not to give rise to visible colour, but it may be compared not unreasonably with the blue or green colour produced by the analogous chromophore $-N=O$ in compounds such as *ter*-nitrosobutane.

The introduction of a second $-C=O$ group in compounds such as methyl methylcamphocarboxylate, $C_8H_{14}\begin{cases}C(CH_3)CO.OCH_3\\|\\CO\end{cases}$, does not intensify the band, as the two carbonyls are not copulated owing to the fact that they are separated by two single linkages instead of one. In camphorquinone, $C_8H_{14}\begin{cases}C=O\\|\\C=O\end{cases}$, on the other hand, the band is brought right into the visible region at 1/2050, and its persistence is increased from log. thickness 0·3 to 1·6; the penetration of the band is, however, practically the same as in camphor, log. thickness 2·6, the decrease in the frequency of the maximum absorption being accompanied by no marked increase in its intensity. The decrease of frequency gives rise to what Schutze has called a "deepening" of colour, an effect which he has conveniently described as "bathochromic," in contrast with the "hypsochromic" action of compounds which cause an increase of frequency and a "lightening" of the colour.

In methylene camphor, $C_8H_{14}\begin{cases}C=CH_2\\|\\C=O\end{cases}$, the introduction of the second unsaturated group produces an entirely different effect, the frequency of the band being unaltered, but its penetration increased to log. thickness 1·7. The copulation of the two groups is thus accompanied by an actual increase of specific or local absorption, an effect which may be regarded as genuinely "auxochromic."

A further increase of penetration to log. thickness 0·3 is produced by the introduction of a third unsaturated centre as in benzylidene camphor, $C_8H_{14}\begin{cases}C:CH.C_6H_5\\|\\CO\end{cases}$, and the derivatives of oxymethylene camphor, $C_8H_{14}\begin{cases}C:CH.OR\\|\\CO\end{cases}$.

The nature of the substituent radicle R in the enolic compounds,—

* Report of the Committee, consisting of Professor H. E. Armstrong (Chairman), Dr. T. M. Lowry (Secretary), Professor Sydney Young, Dr. C. H. Desch, Dr. J. J. Dobbie, Dr. M. O. Forster, and Dr. A. Lapworth. (Drawn up by the Secretary). Read before the British Association (Section B), Sheffield Meeting, 1910.

(*a*) $C_8H_{14}\begin{cases}C:CX.OR\\ |\\ CO\end{cases}$ and (*b*) $C_8H_{14}\begin{cases}C.CO.\\ ||\\ C.OR\end{cases}$,

has no marked influence on the penetration, but the frequency of the band decreases by about 200 units when sodium is substituted for hydrogen or methyl, whilst an increase of similar magnitude results from the displacement of hydrogen by acetyl; the bridging of the ethenoid linkage, which is the main difference between the enolic formulæ (*a*) and (*b*), is accompanied by a decrease of frequency.

WAVE-LENGTH MEASUREMENTS IN THE VISIBLE PART OF THE ARC SPECTRA OF THE ELEMENTS ALDEBARANIUM AND CASSIOPEIUM DISCOVERED BY AUER v. WELSBACH.

By JOSEF MARIA EDER and EDUARD VALENTA.

In addition to our wave-length measurements in the visible part of the spark spectra (Eder and Valenta, *Sitzungsber. d. K. Akad. in Wien*, 1909, vol. cxviii., II. A, pp. 511 and 1078), relating to the spark spectra of air, aluminium, antimony, barium, lead, cadmium, chromium, calcium, iron, gold, indium, cobalt, copper, lanthanum, lithium, manganese, molybdenum, nickel, silver, strontium, tantalum, tellurium, thallium, titanium, vanadium, bismuth, tungsten, zinc, tin), we have also examined a number of arc spectra in the red to greenish yellow spectral regions, which we needed for our "Atlas of Typical Spectra." A very valuable collection of exceedingly pure preparations of rare earths which we owed to the kindness of Herr Auer v. Welsbach, enabled us to extend our investigations to the hitherto unknown long wave-length arc spectra of cassiopeium, aldebaranium, thulium, erbium, neoholmium, dysprosium, yttrium, terbium, gadolinium, europium, samarium, &c. (The ultra-violet arc spectra of erbium, gadolinium, thulium, holmium, europium, ytterbium—mixture of aldebaranium and cassiopeium—have been investigated by Exner and Haschek, "Wave-length Tables"). These spectra often show a simpler structure in the less useful part of the spectrum and are of great interest from a physico-chemical point of view; they could also be used to ascertain the degree of purity of this exceedingly intricate group of the rare earths and of the elements contained in it.

The "element" ytterbium separated by Marignac in 1878 from other rare earths of the yttrium series was approximately measured by Thalen (1881) ("Oefversigt. K. vetensk. Akad. Förhandl," 1881; *Comptes Rendus*, xci., 326; Watts, "Index of Spectra," Manchester, 1889, p. 155) in the visible part of the spark spectrum, and its arc spectrum was accurately studied by H. Kayser in 1903 ("Das Bogenspektrum des Yttriums und Ytterbiums," *Abhndlg. d. Kgl. Preuss. Akad. d. Wissensch.*, 1903).

Auer v. Welsbach succeeded in decomposing ytterbium into two elements which he called cassiopeium (Cp) and aldebaranium (Ad); using a spark-at-break spectrum he proved the individual character of both elements by spectral analysis. The arc spectrum of Cp and Ad in the visible part was unknown, but as in these regions both elements have bright and characteristic spectra we investigated the arc spectra from the light green (λ = 5476) to λ = 7126, using our large grating spectrographs, and determined the wave-lengths of the sharp lines. (We used Schleussner's silver bromide gelatin plates of length 50 cm., which we poured on to very thin flexible glass, and which we ourselves sensitised by a bath of pinacyanol solution). We employ Auer's nomenclature, although there is a tendency to use Urbain's names for these new elements. Auer v. Welsbach's claims to priority in the discovery of the decomposition of ytterbium into two new elements extend back to the year 1905, while Urbain did not publish his article on the separation of ytterbium until 1907. In consideration of this undoubted priority Auer should have the right to provide names for his new elements, for which reason we employ the names cassiopeium and aldebaranium to denote them.

Our wave-length measurements are referred to Rowland and Kayser's standard. The intensities are denoted by the numbers 1 to 10, higher numbers approximately representing the intensities of the brighter lines, while some specially bright lines are given numbers above 10. The two spectra may be described as follows:—

Cassiopeium.

Cassiopeium gives in the red to yellowish green part of the arc spectrum a number of very bright highly characteristic lines which were previously unknown. With a few milligrms. of cassiopeium chloride we succeeded in getting a photograph of this spectral region in the large grating spectrograph, thus obtaining a large number of lines. In the spark spectrum Auer v. Welsbach observed the Cp lines λ = 6222·0, 6160·20, 5984, 5476·94. We found the same lines in the arc spectrum, together with a number of others which undoubtedly belong to cassiopeium. Table I. gives the lines we measured.

Table I.

λ.	i.	λ.	i.
5476·94	30	6199·86	8
5535·70	1	6222·06	20
5602·75	1	6228·34	4
5665·08	2	6235·56	7
5690·27	1	6242·57	10
5700·33	1	6247·20	1
5713·70	3	6249·08	2
5736·73	4	6345·59	5
5775·57	4	6355·15	2
5800·78	8	6366·18	3
5860·99	8	6441·34	2
5866·46	2	6444·07	1
5887·51	1	6463·31	20
5983·85	10	6477·92	2
5984·33	10	6497·19	1
5997·36	6	6523·45	6
6004·74	10	6611·53	2
6041·84	2	6611·97	2
6055·24	6	6619·37	1
6084·39	3	6677·37	1
6141·01	1	6708·04	2
6141·95	1	6794·26	1
6160·17	7	6917·59	2
6195·34	1	7126·23	1

The most characteristic cassiopeium lines are:—λ = 5476, 5736, 5983, 5984, 6004, 6160, 6199, 6222, 6235, 6242, 6463.

It is noteworthy that with a short time of illumination with our preparation *only* these lines appeared, but with a longer illumination the principal lines of aldebaranium also appeared; thus the latter had not been completely removed. In one fraction which contained a mixture of thulium and aldebaranium, cassiopeium was altogether absent.

Aldebaranium.

The oxide, sulphate, and chloride all give the same arc spectrum between carbon electrodes; the red and yellow lines appear more clearly when the salts are used than with the oxide. The arc spectrum of aldebaranium is specially bright and characteristic in the less refrangible part. Auer v. Welsbach investigated the spark-at-break spectrum of aldebaranium only as far as λ = 5897 (these *Sitzungsber.*, vol. cvi., II. B, December, 1907, p. 1425), and mentioned the spark lines λ = 5556·6, 5588·66, 5652·16, 5730·20, 5771·94, 5819·54, 5837, 5897·56 in the region investigated by us. The arc specrum of aldebaranium in the red and yellow was as yet unknown. We found the lines in Table II. in the red to yellowish green parts of the spectrum of aldebaranium (wave-lengths referred to Rowland and Kayser's Standard).

Table II.

λ.	i.	λ	i.
5474·24	1	5803·68	1
(5478·73	1 Tu)	5819·64	2
5482·15	8	5834·20	3
5505·71	3	5837·32	8
5524·68	1	5838·96	1
5539·33	10	5854·72	3
5547·38	1	(5895·88	5 Tu)
5556·71	20	5897·42	2
5562·33	2	5899·00	1
5568·37	1	5908·56	2
5578·45	1	5935·28	1
5581·02	1	5946·31	½
5586·57	1	(5971·50	1 Tu)
5588·67	6	5991·73	4
(5631·62	4 Tu)	6048·70	½
5638·03	1	6053·17	1
5652·21	8	6054·77	1
(5676·09	5 Tu)	6059·45	1
5684·96	1	6152·77	5
5686·75	1	6247·16	4
5690·15	1	6260·99	1
5700·16	1	6274·98	5
5710·17	1	6308·36	2
5713·96	1	6400·60	3
5720·23	10	6418·16	2
5729·13	½	6432·94	2
5730·25	10	(6460·50	1 Tu)
5746·03	1	6489·30	15
5750·10	1	6643·74	1
5756·11	1	6668·04	6
(5764·51	3 Tu)	6727·80	1
5767·39	1	6799·87	10
5771·86	5		

In our aldebaranium spectrum the following strong Cp lines occurred :—λ = 5476, 5736, 6463 owing to its presence as an impurity. If the time of illumination is longer still fainter cassiopeium lines appear.

Moreover, we found in our aldebaranium spectrum the thulium lines, which are enclosed in brackets in the above table. They were sometimes fairly bright. The very characteristic principal lines of aldebaranium in this region are λ = 5482, 5539, 5556, 5652, 5720, 5730, 5837, 6152, 6274, 6489, 6668, 6799. The last named are very bright, and reveal the smallest traces of aldebaranium.—*Sitzungsber. d. K. Akad. d. Wissensch. in Wien*, Math. Sc. Class, cxix., II. A, January, 1910.

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,*

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, &c.

By PERCY H. WALKER.

(Continued from p. 131).

Paints (*continued*).

Coloured Pigments.

4. *Green Pigments.*—The most important green pigment is chrome green, which is a mixture of Prussian blue and lead chromate. A green made of ultramarine and zinc yellow is occasionally encountered. If absolute permanence is required chromium oxide (Cr_2O_3) is sometimes used, but this pigment is not common. The very brilliant copper arsenic compounds (Paris green, &c.) are little used in paints. (For methods of analysis see U.S. Dept. Agr., Bureau of Chemistry, *Bull.* 107, Revised, pp. 25—30; also Lunge, Chemisch-technische Untersuchungsmethoden, ii., 807).

(a) *Chrome Green.*—(1) *General Discussion.*—A pure hrome green should contain only Prussian blue, lead chromate, and lead sulphate. Any other substances should be considered adulterants. Greens made by precipitating the ingredients together are superior to those made by mixing the blue and yellow after they are precipitated separately. To distinguish the two, rub up the pigment in oil and allow to stand. A badly made green will show blue, but one properly made by precipitation will not. A microscopic examination of the dry pigment should also be made. A badly made green will show yellow and blue particles, as well as green. A well-made green will show green and some blue particles, but no yellow. As different grades of lead chromate vary greatly in shade, and as the same is true to a somewhat less extent with Prussian blue, actual determinations of the percentages of Prussian blue, lead chromate, and lead sulphate are of little real value, and the analysis of chrome green is made with difficulty. It is, however, important to determine impurities, which may be barium sulphate, silica and silicates (clay), or calcium and magnesium compounds. (2) *Impurities.*—To examine for impurities proceed as follows :—Place 1 grm. in a small casserole, add 10 cc. of water and sodium peroxide, a little at a time (about 1 grm. in all), to oxidise the Prussian blue; add about 25 cc. more of water and boil for some time, so as to decompose all of the hydrogen peroxide. Acidify with hydrochloric acid, boil, filter, and wash. Transfer the residue again to the casserole and boil with a solution of ammonium chloride (slightly alkaline) to dissolve the last trace of lead; filter, wash, ignite, weigh the insoluble impurities, and determine their nature. They are probably barytes or silica. Heat another 1 grm. portion very gently in a casserole or small porcelain dish, and remove from the flame as soon as it begins to glow. The heating should be carried out very carefully, the object being to decompose the Prussian blue but not to heat it enough to render the iron difficultly soluble. Allow to cool, add hydrochloric acid, and digest covered on the steam-bath for an hour. As a general rule this treatment brings everything except insoluble impurities into solution. Cool, dilute to 300 cc., and pass in a rapid stream of hydrogen sulphide until all of the lead is precipitated; filter, wash with water containing some hydrogen sulphide, boil off the hydrogen sulphide from the filtrate, add bromine water to oxidise the iron, add ammonium hydroxide in slight excess, filter, dissolve the precipitate in hydrochloric acid, re-precipitate with ammonium hydroxide, filter, wash, unite the filtrates, and determine calcium and magnesium in the usual way. (3) *Quantitative Determination of Yellow and Blue.*—The examination for impurities is usually sufficient, but if a quantitative determination of yellow and blue be desired, the sulphate may be determined in the united filtrate from the insoluble impurities by precipitating from hydrochloric acid with barium chloride. The ferric ferricyanide present will not cause any difficulty if the barium sulphate is filtered off soon after precipitating; but if it is allowed to stand a long time a reduction is likely to take place with the re-formation of some Prussian blue. Determine the lead in the second portion by dissolving the lead sulphide in nitric acid, boiling the residues with ammonium acetate, uniting the filtrates, adding sulphuric acid, heating to fumes, and completing the determination of lead as sulphate in the usual manner. For iron and chromium dissolve the ammonia precipitate in hydrochloric acid, make up to definite volume, determine the iron in an aliquot by reduction and titration with potassium permanganate or potassium dichromate. Determine the chromium in another aliquot as described under chrome yellow. (4) *Miscellaneous Determinations.*—If aluminium is present, precipitate another aliquot with ammonium hydroxide, wash, dry, ignite, and weigh. From the iron and chromium determinations calculate the combined weight of ferric oxide and chromium oxide and obtain aluminium oxide by difference. Determine the moisture and the nitrogen as described under Prussian blue. If the presence of ultramarine is suspected, test with hydrochloric acid, and if hydrogen sulphide is evolved, ultramarine is present.

* *Bulletin* No. 109, Revised, U.S. Department of Agriculture, Bureau of Chemistry.

(b) *Ultramarine and Zinc Yellow Green.*—(1) *General Discussion.*—No lead compounds should be in this green, since with lead and ultramarine the paint will soon be blackened by the formation of lead sulphide. Owing to the widely varying composition of ultramarine, it is not possible to make a quantitative determination of the blue, but its presence can be detected by means of hydrochloric acid, and the combined percentage of ultramarine and insoluble impurities thus be determined. (2) *Determination of Yellow.*—Treat 1 grm. of the dry powder with 25 cc. strong ammonium hydroxide, stir well, and dilute to about 100 cc. with water. Stir frequently for about thirty minutes, carefully breaking up all lumps, but do not heat. Filter, wash with dilute ammonium hydroxide, and then with water; dry the residue at 105° C. to constant weight, and weigh. The loss in weight gives the amount of zinc yellow if no other soluble compounds are present. The filtrate may be tested as in the examination of zinc yellow. (3) *Ultramarine and Insoluble Impurities.*—The insoluble material remaining from the determination of yellow (2) may contain both ultramarine and other insoluble substances, but its colour strength can be determined as compared with a standard pure ultramarine, and the result calculated to percentage based on a standard ultramarine.

Mixed Paints.

Single pigments are generally sold either dry or ground in oil alone; rarely do they contain thinners or dryers. Ready-mixed paints, however, contain, in addition to oil, turpentine or gasoline and usually some dryer. More complicated yet are enamel paints, which are pigments ground in oil varnish, and contain, beside the substances in the vehicle of mixed paints, varnish gums.

The can of mixed paint should not be shaken, but should be weighed as a whole, opened, and as much of the clear vehicle removed as possible; this should be weighed and kept in a stoppered flask (use cork, not rubber, stopper). After removing the clear vehicle mix the contents of the can thoroughly and transfer to another jar. Wipe and weigh the can. These figures will give the necessary data for calculating the analytical results back to the original material.

1. *Extraction of the Vehicle.*—Weigh from 15 to 35 grms. of the thoroughly mixed pigment in a tall, narrow Erlenmeyer flask of 300 cc. capacity. Add about 10 cc. of gasoline, mix thoroughly, then add 150 cc. of gasoline, mix well, and stopper with a cork; allow to stand until the pigment has settled, and decant the liquid into a beaker; some pigment will frequetly go over with the gasoline, so it is well to allow this to settle and decant into a second beaker. Repeat the treatment with gasoline; after the first treatment settling is generally much more rapid. Decant the gasoline as completely as possible the second time. Then add 150 cc. of benzol (C_6H_6), shake, and allow to settle. Decant the benzol and treat in same way with 150 cc. of ether. (If a large number of samples are examined at the same time this method is as rapid as any; but when working with a small number of samples much time is saved by extracting in tubes and throwing down the pigment by whirling in a centrifuge). This method of extraction is often more satisfactory than any method using a continuous extraction apparatus, for frequently the pigments can not be held by extraction thimbles. This method of treatment will generally give an almost complete separation of the vehicle, but in some enamel paints it is well to follow the gasoline treatment by a treatment with turpentine, and then remove the turpentine with gasoline before treating with benzol and ether. Some paints are very difficult to settle when treated with a single solvent, and mixtures of solvents must then be tried. Mannhardt (Select Methods of Paint Analysis) recommends 60 volumes of benzol and 40 volumes of 95 per cent wood alcohol. No system of extraction will remove absolutely all the vehicle, the insoluble portion being probably metallic soaps or linoxyn. After removing all of the soluble vehicle, dry the pigment, first at a low temperature in a gentle current of air, and then at 105° C.; weigh, and from the loss in weight calculate the percentage of vehicle and pigment; then from the total weight of mixed paint and the weight of clear vehicle drawn off calculate the percentage of vehicle and pigment in the original paint.

2. *Analysis of Pigment.*—Follow the methods for dry colours. In general determine the amount insoluble in hydrochloric acid and the nature of the insoluble, and make an analysis of the soluble portion. In the absence of carbon and hydrated silicates (clay, &c.), a fairly close determination of unextracted vehicle may be made by drying the insoluble at 105° C., weighing, and then igniting and weighing. This loss is called combined water and carbonaceous matter, and in many cases may be safely considered as unextracted vehicle.

3. *Analysis of Vehicle.*—Weigh 100 grms. of the vehicle into a 500 cc. flask, connect with a spray trap and a vertical condenser, and pass through it a current of steam, first heating the flask in an oil-bath at 100° C.; with the steam still passing through, raise the temperature of the bath to 130°. Catch the distillate in a small weighed separatory funnel; continue distillation until the funnel contains 300 cc. of water. Let the distillate stand until separated into two layers, then draw off the water and weigh the light oils. Examine as under Turpentine (*ante*). A slight error is caused by the solubility of turpentine in water; this amounts to about 0·3 to 0·4 cc. for each 100 cc. of water. When sufficient vehicle is available it is well to take another portion and distil, without steam, placing the flask in an air-bath. Note the temperature of the bath at which distillation takes place, and continue the distillation at a temperature of 185° C. in the air-bath. This method gives somewhat lower results on volatile oils than the first method, but the distillate can be tested for water-soluble volatile liquids which would be lost by the steam distillation. Unsaponifiable matter should be determined in this residue, or in some of the original vehicle. (See Examination of Linseed Oil). The residue is frequently too pasty for the determination of the specific gravity, which should be made on the original vehicle. Determine specific gravity with a plummet or hydrometer. The small amount of suspended pigment which frequently remains in the vehicle will introduce an error when a pyknometer is used. Determine the acid number of the residue and of the original vehicle. Determine the percentage and the character of the ash either from the residue or the original vehicle. The iodine number is sometimes a useful index; but the constants of linseed oil which has been mixed with pigments, especially lead compounds, may be so much altered that an iodine number as low as 100 can not be taken as any proof of the presence of other fatty oils. Test for rosin as described under Linseed Oil. Another test for rosin may be made by dissolving in carbon disulphide and adding a solution of stannic bromide or chloride in carbon disulphide. Use a white porcelain dish. If no water is present in either solution the presence of rosin is shown by the appearance of a violet colour. This test is not as delicate as the Liebermann-Storch test described under linseed oil. When much lead is present it may be lost in ashing, and for a correct determination of metals the following method is best:—Place 25 grms. of the vehicle in a 500 cc. separatory funnel, dilute with 25 cc. of a mixture of equal parts of gasoline and turpentine, add 50 cc. of nitric acid (1 : 1), and let stand one hour, shaking every ten minutes. Then immerse the funnel in hot water, loosen the stopper, and shake gently. This drives off nearly all the gasoline. Remove from the hot water, let it separate, draw off the lower layer, and wash the upper oily layer four or five times with warm water. Add the washings to the main acid portion and determine the metals in the ordinary manner. If the paint is enamel paint, treat the vehicle as a varnish (see *ante*).

To be continued).

THERMIC REACTIONS *IN VACUO*.*

By FRANK E. WESTON, B.Sc., and H. RUSSELL ELLIS, B.Sc.

Part I.

In a paper read before the International Congress of Applied Chemistry, in June, 1909, the authors gave a synopsis of a number of reactions similar in nature to the well-known "Thermite" reaction, and also an account of experiments carried out with these mixtures *in vacuo*. As the paper appears only in abstract in the *Proceedings* of the Congress, and as the work has been further extended since that time, it was thought advisable to give further details.

The authors are only able to find reference to two attempts where similar reactions have been tried *in vacuo*. Pring (*Journ. Chem. Soc.*, 1908, 2108) heated Al and C in an electric vacuum furnace and found that at 640° C., the melting-point of Al, combination begins to take place and that at 1400° C. it proceeds rapidly. From the description of the experiment it appears that the reaction once started does not proceed throughout the mass, whereas, as shown by the authors, a mixture of 4Al and 3C when ignited with a fuse commences to react and proceeds throughout the mass, when the reaction is carried out in a Hessian crucible in the air.

Watts and Breckenridge (*Trans. Am. Elect. Soc.*, 1908, xiii., 103) state that they were able partially to reduce silica by means of an alloy of Mg-Ca-Al when the mixture was heated in a steel vacuum tube to a high temperature; also that a mixture of MnO_2 and SiO_2 when heated with the same alloy in the steel vacuum tube produced an alloy of Si-Mn (22 per cent of the theoretical yield).

It thus appears from these isolated cases that certain "Thermitic" reactions which take place readily in the air are only partially reproduced *in vacuo*, and only then when continuously heated to a high temperature.

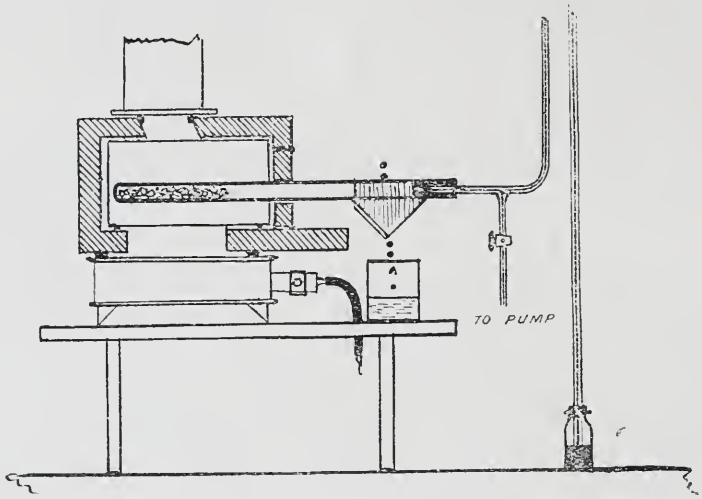


Fig. 1.

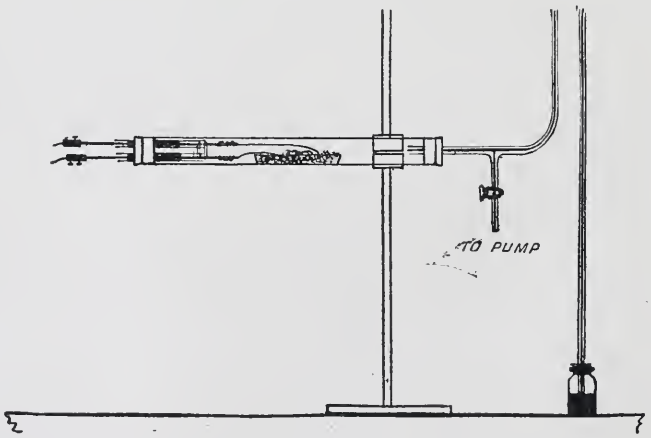


Fig. 2.

Experimental Methods.

The following methods have been used by the authors with varying degrees of success.

Method 1.—The mixture is placed in a mild steel test-tube, 18 in. long by ½ in. diameter; the tube is connected both to a mercury manometer and a Töpler pump. It is heated in a Fletcher muffle furnace to a temperature of 1100° C. The projecting part of the test-tube is cooled by cold water in order to preserve the connection between the steel tube and the glass tube; the cementing material con-

* A Paper read before the Faraday Society, May 31, 1910.

sisted of an intimate mixture of fine asbestos wool, litharge, and water-glass (see Fig. 1).

1. Mixtures of Mg and Al_2O_3 when heated in this apparatus reacted with explosive violence.

2. Mixtures of Mg and CaO when heated in these tubes did not react, but the Mg distilled from the mixtures and condensed in the cool part of the tube. After several trials with different mixtures it was found that the method of heating the mixtures was unsatisfactory and so the method was abandoned.

bedded in the mixture, a channel was immediately formed on heating the wire.

2. Thermite reacted in this apparatus, but invariably broke the tube.

3. All mixtures of Al and Na_2O_2 tried reacted with separation of metallic Na, but invariably broke the tube.

Method 3.—After several trials with small bottles, using Pt wire and Fe wire as the initial source of heating, it was found that certain fuses could be easily fired by Fe wire heated by an electric current, and finally, the following

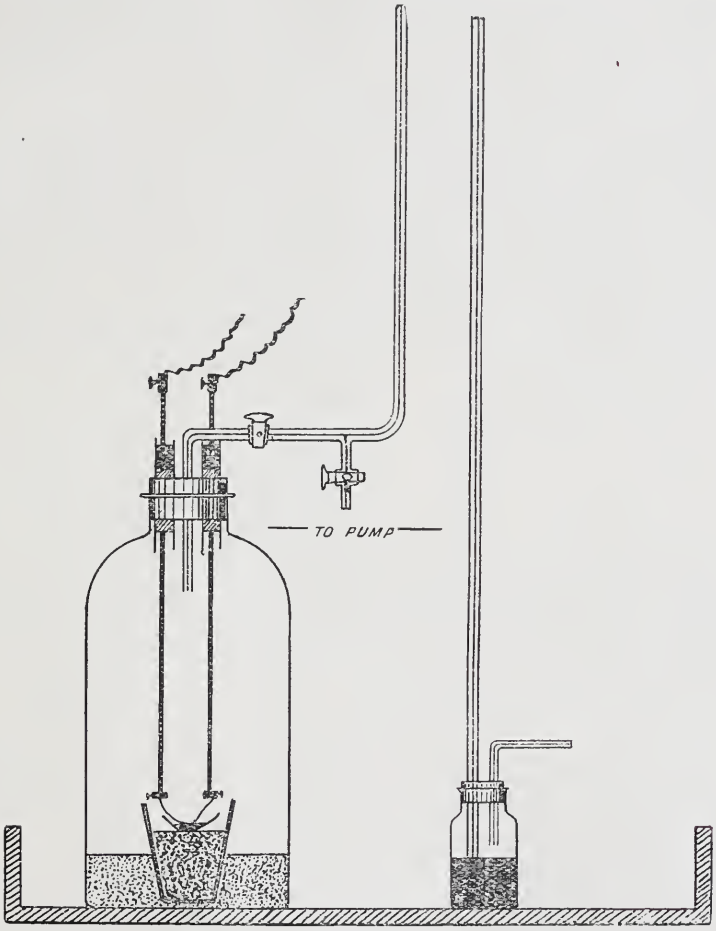


Fig. 3.

Method 2.—The mixture, contained in a porcelain boat, was placed in a Jena glass tube 12 in. long by 1 in. internal diameter (see Fig. 2). A coil of thin platinum wire lying in the mixture was connected to two stout copper wires, which were embedded in glass tubes to the length of about 6 in. by means of Faraday's cement; these tubes passed through a rubber cork and could be connected to a source of electric current. The other end of the Jena tube was connected to a mercury manometer and the Töpler pump.

It was very soon ascertained that the heat produced in the Pt wire by the passage of the electric current was insufficient to start the reaction of the mixtures, even when the Pt was raised to its melting-point (1780° C.), except in a very few cases, and then the tube invariably broke through the sudden great evolution of heat, *e.g.*—

1. Mixtures of Mg and CaO were repelled from the heated Pt wire, and even when the Pt wire was well em-

apparatus was designed and found to give the best results.

A wide-mouth bottle of three litres capacity was fitted with a rubber cork carrying three glass tubes; two of these tubes carried stout copper wires, which were embedded in Faraday cement for a length of 6 in. and at the top end in 2 in. of paraffin wax. The third tube was connected to a Töpler pump and a mercury manometer (see Fig. 3).

The bottom of the bottle was covered with a layer of sand mixed with small lumps of quicklime—this mixture had been previously heated in a muffle furnace and finally cooled in a desiccator. A Hessian crucible holding from 20 to 30 grms. of any of the mixtures was embedded in the sand, and on top of the mixture was placed 0·1 grm. of the fuse contained in a very thin piece of tissue paper; on inserting the cork, a loop of very thin iron wire, connected to the two copper leads, just lay embedded in the fuse. The jar was first exhausted with a water-pump, and then

finally by a Töpler pump; then the fuse was fired by passing an electric current through the iron wire from one to two seconds. The reactions that took place always did so quietly and steadily. In no case did the crucible crack and a very small amount of the mixture was always left unchanged. The pressure in the apparatus, after the reaction was completed, was usually from 50 to 80 mm.—due to combustion of the piece of paper used with the fuse.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cli., No. 2, July 11, 1910.

Density of Radium Emanation.—Sir William Ramsay and Robert Whytlaw Gray.—The most conclusive way to establish the atomic weight of a gaseous element is to determine its density. If the element is monatomic both the atomic and molecular weight are obtained by doubling the density. Radium emanation is without doubt one of the inert gases, and it is only necessary to find its density in order to fit it into the Periodic Table. This the authors have done by direct weighings, using a quartz balance (sensitive to half a millionth of a milligrm.). The following table gives the results of five determinations:—

Vol. of em. weighed at 0° and 760 mm. in thousand of a cubic mm.	Wt. of emanation in millionth of a mg.	Molecular weight.
72·8	722	222
58·5	564	216
58·5	577	227
67·7	658	218
73·0	706	217
	Mean	220

Thus the emanation is the second member of the series of inert gases, after xenon. Since it is undoubtedly an element its former cumbrous designation might conveniently be dropped, and the authors suggest as a suitable name Niton (shining), symbol Ni.

Critical Constants of Acetylene and Cyanogen.—Ettore Cardoso and Georges Baume.—The mean values of the critical constants of acetylene and cyanogen are as follows:—

$C_2H_2.t_c = 35{\cdot}5^\circ$ (308·5 abs.), $p_c = 61{\cdot}5$ at.
$C_2N_2.t_c = 128{\cdot}3^\circ$ (401·3 abs.), $p_c = 59{\cdot}6$ at.

Determination of Methylamine in Presence of Large Amounts of Ammonia. — J. Bertheaume. — Methylamine replaces ammonia in its salts, and this property can be used as the basis of a method of determining it in presence of large quantities of ammonia. The mixed gases are led through a series of flasks containing hydrochloric acid, and thus the amines are concentrated in the first flasks.

Fixation of Trioxymethylene by the Magnesium Derivatives of the Homologues of Benzyl Bromide. —P. Carré.—The bromide of mesityl magnesium reacts with trioxymethylene in the same way as the chloride of benzyl magnesium, giving mesitylcarbinol and a fairly large proportion of the corresponding ether oxide.

No. 3, July 18, 1910.

Action of Ultra-violet Rays on Gelatin.—A. Tian. —The ultra-violet rays do not appear to have any action on gelatin nor on its dilute solutions. The same rays destroy gels, causing their liquefaction or, in presence of water, their solution. The waves producing these changes have wave-lengths below 3000 A. Thus they belong to the same spectral region as those which coagulate the albumens.

Relative Duration of Calcium Rays in the Self-induction Spark.—G. A. Hemsalech.—The results of the investigation of the duration of calcium rays confirm the conclusion drawn from the iron rays, viz., that the duration is approximately proportional to the intensity. In some cases the duration of the rays indicates the nature of the impurities present in a substance. The author thus found that the calcium he used contained traces of strontium, magnesium, aluminium, and manganese.

Photographic Method of Counting α-Particles.—William Duane.—The author describes a method of counting the α-particles emitted by a radio-active substance. The particles enter the ionisation chamber through a thin wall of mica, and the ionisation due to each particle is registered by means of a sensitive electroscope or a quadrant electrometer. A photographic record of the movements of the gold leaf enables the effect of each particle to be seen.

Thorium Sulphate.—M. Barre.—The specific resistance and the freezing-point of thorium sulphate in aqueous solution agree perfectly with the laws of Bonty and of Raoult. The measurement of the conductivity and of the freezing-point of solutions containing 1 per cent of potassium sulphate indicate the formation of a stable double salt, and thus the results of determinations of the solubility are confirmed.

Action of Ether Salts of Fatty Monobasic Acids on the Monosodium Derivative of Benzyl Cyanide.—F. Bodroux.—When the ether salts of monobasic fatty acids act on the monosodium derivative of benzyl cyanide substances of formula $C_6H_5—\underset{\displaystyle CN}{\underset{|}{CH}}—CO—R$ are obtained. The author has prepared and investigated the properties of some of these nitriles, *e.g.*, phenylpropanal nitrile. They are unstable bodies which decompose in dilute alkaline solution at the ordinary temperature.

Absorption of Iodine by Solid Substances.—Marcel Guichard.—The fixation of iodine at the surface of a solid is a specific property, and many substances exhibit the property to a very slight extent only. The power of absorption varies with the circumstances and with the preparation of the solid in question.

MISCELLANEOUS.

Birkbeck College.—The 88th Session of the College will commence on Wednesday, September 28th. The Opening Address will be given in the Theatre, at 7.30 p.m., by Prof. M. E. Sadler, M.A. The Class Rooms, &c., will afterwards be open for inspection, and there will be an Exhibition in the Art School. Visitors are invited. The College is conducted in relation with the University of London; Classes are held both in the Day and Evening; twenty-nine Members of the Staff are Recognised Teachers of the University. The courses of study provides for Degrees in the Faculties of Arts, Science, Laws, and Economics. There is a very complete curriculum for Chemistry, Physics, Mathematics, Botany, Zoology, and Geology, The Laboratories are well equipped with modern apparatus and appliances, and Research Work is encouraged in all the Science Departments. The Arts Courses include English, Classics, French, German, Italian, History, Logic, Mathematics, Economics, and Geography, all conducted by Recognised Teachers of the University. The Law Courses comprise Mercantile and Common Law, Equity, Conveyancing, and Patent Law, Classes in English and Roman Law, and Constitutional Law and History. According to the Calendar more than 140 Students passed some Examination of the University during the last Session; forty-five took Degrees in Arts or Science, twenty with Honours, and several Students gained distinction at other Universities. The College possesses an Art School, which provides instruction in the various Branches of Artistic Work (Painting, Modelling, Life, Design, &c.).

THE CHEMICAL NEWS.

Vol. CII., No. 2653.

SCANDIUM.*

Part II.†

By R. J. MEYER and HERBERT WINTER.

Occurrence and Preparation in the Pure State.

In the first article on scandium, to supplement G. Eberhard's spectrographic experiments (*Sitzungsber. Kgl. Preuss. Akad. Wissensch.*, 1908, xxxviii., 851), new methods were described which had led to the separation of scandium from the wolframite of the Ore Mountains in Saxony. These methods essentially depended upon the insolubility of scandium fluoride in presence of free mineral acid, and upon the fact that scandium can be precipitated with sodium thiosulphate. (See also D.R.P. 202523 and 208355, Class 40 A, Group 51). The initial material consisted principally of the residues of iron and manganese oxide, which remain undissolved after boiling up the alkaline melt of wolframite. If this mixture of oxides is dissolved in hydrochloric acid, so that a nearly neutral solution is obtained, the rare earths contained in the wolframite can be precipitated from this solution by means of a large excess of oxalic acid. The precipitate also contains manganese, calcium, iron, and lead oxalates. To purify it further, this product in which the scandium has accumulated is precipitated in acid solution with hydrofluoric acid. A second and simpler method consists in the direct precipitation of the hydrochloric acid solution of the original mixture of oxides with sodium silicofluoride. When fresh scandium has repeatedly to be prepared from wolframite residues this method is found very convenient. The hydrofluosilicic acid separates the earth in a very pure state, and it is preferable to employ this process rather than the combined oxalic acid and hydrofluoric acid method, *when the object is to obtain the scandium alone.* But if all the earths of wolframite are to be studied it is essential to perform the separation with oxalic acid. We have recently given special attention to the qualitative and quantitative composition of the earths contained in wolframite, and have found that the relative amount of scandium oxide in it is not so high as was supposed when these circumstances were not taken into consideration.

For further investigation we used a raw scandium oxide which had been obtained only by repeated oxalic acid precipitations from the solution of the oxide residues, and which must thus contain all the rare earths of the wolframite. It was a yellowish powder, the solution of which in hydrochloric acid on spectroscopic examination showed very faintly the principal bands of didymium. The cerium reaction was correspondingly faint, but the bands of the erbium earths appeared fairly clearly. Thus it was a mixture of earths, consisting essentially of yttrium earths.

The examination of the arc spectrogram by Prof. G. Eberhard‡ showed that, besides scandium, yttrium was the chief constituent. If the scandium is precipitated from the solution of these earths with sodium thiosulphate, from the thiosulphate precipitate a pure white oxide can be obtained; in it are accumulated all the scandium and the small amounts of thorium which the raw earths contained, while all the cerite and yttrium earths which are not separated with thiosulphate are found in the filtrate. This separation is almost quantitative, as we have repeatedly found. No trace of scandium remains in the filtrate; the precipitate contains only a very small amount of yttrium earths which can be removed by repeated precipitation with thiosulphate (*cf.* pp. 147—149 of the first article). When this separation was carried out quantitatively 44 grms. of rare earths gave 22 grms. of Sc_2O_3 (with small amounts of ThO_2), and 17 grms. of yttrium earths; the residue of 5 grms. consisted of iron, manganese, calcium, lead, &c.; apart from these "not rare earths" the mixture of earths of wolframite from Zinnwald consists of 56·4 per cent Sc_2O_3 and 43·6 per cent of other rare earths. The mixture of oxides obtained by direct precipitation with sodium silicofluoride is much richer in scandium. To investigate it 48 grms. of the nearly pure white product were converted into chloride and precipitated with sodium thiosulphate. In the filtrate 3·2 grms. of yttrium earths were dissolved. Hence the oxide from the silicofluoride precipitation contains 93·3 per cent Sc_2O_3 and 6·7 per cent of other earths.

For completeness sake the quantitative analysis of the wolframite from Zinnwald is given below. The material consisted of black glittering pieces with single crystal surfaces. It was carefully picked out for the analysis with a microscope:—

Wolframite from Zinnwald.

	Per cent.	Per cent.
WO_3	75·41	—
FeO	9·34	9·36
MnO	14·00	14·15
PbO SnO_2 ..	0·18	0·35
$TiO_2 + Ta_2O_5$ ..	0·50	0·47
CaO	0·55	0·70
Rare earths ..	0·15	0·15
Sum	100·13	

Thus the Zinnwald wolframite contains about 0·1 per cent of pure scandium earth. Wolframite containing scandium is also found in the Sadisorf Copper Mine near Schmiedeberg in the Ore Mountains (Eberhard, "Uber die weite Verbreitung des Scandiums auf der Erde II.," *Sitzungsber. der Kgl. Preuss. Akad.*, April 21, 1910, xxii., 404). The wolframite from this place differs from that found at Zinnwald-Altenberg in the fact that the proportion of iron to manganese is reversed. The specimens which we had at our disposal could be separated from accessory constituents only with difficulty. Pieces that had not been picked out with sufficient care gave on analysis only about 70 per cent of tungstic acid, and 2 to 2·3 per cent of titanic, niobic, and tantalic acids, some molybdic acid, and a not inconsiderable amount of calcium phosphate. Sadisorf wolframite contains rather more rare earths than that from Zinnwald, about 0·2 per cent being found in it. The amount of scandium may be about the same, but the earth isolated from the Sadisorf mineral with sodium silicofluoride and thiosulphate contains more thorium oxide as the spectrographic examination shows. The following analysis refers to a specimen picked out with the greatest possible care:—

Wolframite from Sadisorf.

	Per cent.
WO_3	73·47
$TiO_2(Nb_2O_5)$	0·63
$PbO + SnO_2$..	0·47
FeO	15·13
MnO	9·81
CaO	0·54
Rare earths	0·20
Sum	100·25

As regards the composition of the oxide residues of the tungsten factory which were used for the preparation of the scandium, we have repeatedly found that they always contained 0·3 per cent of scandium oxide (including small quantities of thorium oxide) if they were obtained from

* *Zeit. Anorg. Chem.*, lxvii., 398

† Part I. of this article appeared in *Zeit. Anorg. Chem.*, 1909, lx., 134; also Chemical News, xcix., pp. 85, 97.

‡ Prof. G. Eberhard, of the Astrophysical Observatory in Potsdam, has rendered great assistance in the second part of the investigation, as in the first, and I take this opportunity of offering him my hearty thanks.

fairly pure ore (Stuferz). The residues from the more impure "Schlicherz" and "Setzerz" are generally much poorer in scandium, corresponding to the smaller amount of tungstic acid in this material. Thus a specimen of wolframite from Zinnwald with 50 per cent of WO_3 gave only 0·04 per cent of Sc_2O_3. On the other hand, we have occasionally come across residues supposed to be derived from slick or small ores which contained the normal percentage (0·3) of Sc_2O_3. The different compositions of these products seem to depend upon accidents of locality, and also upon the kind of preliminary separation and working up. To test rapidly whether a material is worth working up for scandium, the hydrochloric acid solution of 100 grms. of the residue may be boiled with sodium silicofluoride, the precipitate obtained decomposed with sulphuric acid, and the solution of the sulphate residue precipitated with ammonia. The colourless oxide obtained from the hydroxide or oxalate should weigh not less than 0·3 grm. if the quality of the product worked up is good.

As Eberhard has shown, besides certain wolframites from the Ore Mountains, the tinstone accompanying them contains much scandium. We have not studied this material ourselves, but have investigated fairly thoroughly the tin-slacks which are obtained from the slopes, often centuries old, of former tin works in the Ore Mountains. In the slacks obtained from the smelting of Zinnwald ores only the more important constituents were determined analytically. A historical description is given of the method of smelting employed hundreds of years ago in the Inaugural Dissertation by H. Winter, "Vorkommen und Reindarstellung des Scandiums," Berlin, 1910, in which urther information is to be found relating to the analysis of wolframites and tin-slacks.

Tin-slack from Zinnwald.

	Per cent.	
Sn (met.) ..	6·5	13·2 per cent met. tin
SnO_2	8·6	
SiO_2	16·0	
WO_3	30·0	
FeO	18·4	
MnO	9·0	

The residue consists chiefly of calcium phosphate, derived from the fluxes. To determine the amount of scandium present the slack was opened up with soda in an iron crucible, and after the silicic and tungstic acids had been separated with hydrochloric acid the earths were precipitated with oxalic acid or sodium silicofluoride, and then purified by a thiosulphate precipitation. With two different slacks the amount of scandium oxide was found in both cases to be 0·09 per cent, which is about the same as that contained in wolframites. The high percentage of tin in the slacks shows how irrational were the old methods of smelting the tin ores of the Ore Mountains.

The articles of Sir William Crookes (*Proc. Roy. Soc.*, Series A, 1908, lxxx., No. A 541, p. 516; in full in *Phil. Trans. Roy. Soc.*, Series A, 1908, p. 208; translated in *Zeit. Anorg. Chem.*, 1909, lxi., 349; also Chemical News, vol. xcviii., p. 274 *et seq.*) directed our attention to the Finnish wiikite which was said to contain more than 1 per cent of Sc_2O_3. According to the specified composition this mineral must be allied to the euxenites, which, when obtained from Norway, are said to contain 0·06 per cent of scandium earth, as Hauser and Wirth have quite recently stated (*Ber.*, 1909, xlii., 4445). The examination of wiikite, 500 grms. of which we obtained from Herr A. H. Petra, of Helsingfors, gave the astonishing result that hardly any scandium could be detected in it. In agreement with Crookes we found, after the separation of the acid metals (TiO_2, Ta_2O_5, Nb_2O_5) and of the silicic acid, about 13 per cent of rare earths, viz., 9 per cent of cerite and yttrium earths, and 4 per cent of thorium oxide, but scandium could not be detected with certainty in the part precipitated with thiosulphate. The spectrographic examination of the earths also revealed only a small amount of scandium (see Eberhard, *Sitzungsber. d. Kgl. Preuss. Akad.*, 1910, xxii., 413, No. 657 of the minerals examined). In answer to our enquiries, Sir William Crookes then most kindly informed us that the supply of wiikite containing scandium which was extracted for him at a place in Finland was exhausted. But, as appears from the more recent researches of Eberhard (*loc. cit.*), many different minerals, varying in appearance and colour, are often described under the name wiikite, when their chemical nature is not sufficiently well known, and when possibly they belong to different species. They are all found in Finland, on the Northern shores of Lake Ladoga in the parish of Impilaks, and the two most important localities in which they are found are the islands Lokansaari and Nuoliniemi on the coasts (*Bull. de la Commission Géologique de Finlande*, Helsingfors, 1907, No. 19, "Die Erzlagerstätten von Pitkäranta am Ladogasee von Otto Trüstedt"; with a geological chart 1 : 40,090), Among the specimens of these minerals investigated spectrographically by Eberhard (No. 647—656) some contain considerable percentages of scandium. It would be interesting to examine them analytically in order to be able to form an opinion concerning their chemical character and their relations to one another.

Preparation of Pure Scandium. Separation of Thorium.

By using the methods of separation and purification described in the first article, we obtained a raw scandium the atomic weight of which was about 46. The result of the spectrographic and chemical examination showed unmistakably that of known impurities, only thorium was present. Repeated experiments have convinced us that the earth precipitated with sodium silicofluoride, and then repeatedly purified with sodium thiosulphate, no longer contains any foreign yttrium earths; in the arc spectrum neither yttrium nor ytterbium can be detected. This result is all the more remarkable because the ytterbium earths are extremely persistently retained in the last fractions by the scandium earths in the method used by Nilson, Cleve, and Crookes of the fractional decomposition of the nitrates. This may be explained by the very small difference of basicity of the two earths. The problem still to be solved is thus the separation of thorium from scandium. At the end of the first article allusion was made to the difficulty of effecting this separation. Even from a qualitative point of view thorium in presence of a large excess of scandium shows certain deviations from its normal behaviour. Thus it is not possible to precipitate the thorium from scandium containing thorium in neutral solution by means of hydrogen peroxide a reaction which enables thorium to be separated quantitatively from the other earths. By synthetic experiments we have shown that the amount of thorium salt present must be very considerable in order that precipitation with hydrogen peroxide may occur. This hindering of a reaction can only be explained by the well marked tendency of scandium to form strong complexes. We have finally found only one single reaction by which thorium can be detected in presence of scandium with certainty; it depends on the action of iodic acid in strongly acid solution (see R. J. Meyer and M. Speter, *Chem. Ztg.*, 1910, No. 35). The solution in sulphuric acid or nitric acid is treated with an excess of iodic acid in nitric acid. Scandium iodate, which is simultaneously precipitated, is again dissolved if sufficient acid is added, while the very difficultly soluble thorium iodate remains undissolved even in a very great excess of acid. Moreover, very small amounts of thorium in the scandium are revealed by the fact that the neutral solution of the chloride, when it is strongly diluted, becomes turbid after some time, owing to the separation of thorium oxychloride, while solutions free from thorium remain clear.

We will now describe the experiments which were undertaken to separate thorium from scandium.

The initial material for this research consisted of about 70 grms. of scandium oxide of mean atomic weight 48·0.

(Note.—The atomic weights were determined by analysing the sulphate as well as the oxalate, but the number thus obtained does not correspond to the actual composition of the material. Thus, in the calculation $R_2O_3 : 3SO_3$ or $R_2O_3 : 3C_2O_3$ no account is taken of the fact that the chief impurity consists of a tetravalent element thorium. Moreover, the atomic weight determinations of scandium containing thorium, in so far as they are deduced from the relation $R_2O_3 : 3SO_3$, are affected by another analytical error. As R. J. Meyer and A. Gumperz have shown (*Ber.*, 1905, xxxviii., 817), anhydrous thorium sulphate cannot be obtained as a neutral salt by evaporating a sulphuric acid solution of the oxide and heating the residue, so that some of the thorium may be present as acid or basic sulphate. Such determinations therefore give no clear indication of the actual composition, but they are only valuable as providing a check of the progress of the purification operations.

I. *Experiment to Separate Scandium and Thorium by the Extraction of the Ignited Oxide with Hydrochloric Acid.* (Initial Material, $R^{III} = 48{\cdot}0$).—As strongly ignited thorium oxide is almost insoluble in hydrochloric acid, while ignited scandium oxide after long boiling is completely dissolved, even by dilute acid, it occurred to us to try a separation of the two elements based upon this fact. But as a matter of fact, it was found that, on extracting the scandium oxide containing thorium which had been strongly ignited before the blowpipe by boiling long enough with acid, all the oxide could be brought into solution, probably owing to the formation of a double compound, $Sc_2O_3—ThO_2$. But it could be shown that if the boiling was stopped before the last residue of the oxide had dissolved, the thorium had accumulated in the residue, as the following atomic weight determination shows:—The oxide ($R = 48{\cdot}0$) was ignited at a high temperature for a long time, and then extracted by boiling with hydrochloric acid in such a way that an insoluble residue remained. The atomic weight determination in the oxide obtained from the solution by the sulphate method gave:—R_2O_3, 1·1913; $R_2(SO_4)_3$, 3·2090; R^{III}, 46·85. The result shows that a part of the thorium can be removed in this way. But even if after repeated application the method led to the desired result, which is doubtful, it is too tedious and uncertain.

II. *Experiment to Separate Scandium and Thorium with Hydrogen Peroxide.* (Initial Material, 48·0).—As has already been mentioned, small quantities of thorium cannot be separated from a scandium solution by means of hydrogen peroxide in the usual way. The experiment was therefore tried of previously adding to the scandium solution an excess of thorium nitrate, on the supposition that then the addition of hydrogen peroxide would completely precipitate the thorium as peroxide hydrate. But this is not the case, as the following experiment shows:—Two grms. of scandium oxide were dissolved in hydrochloric acid, the chloride solution was made neutral by evaporation, and enough pure thorium nitrate was added to give an abundant precipitate at 60° with pure 10 per cent hydrogen peroxide (prepared from Kahlbaum's perhydrol). It was filtered off, and in the filtrate, which, according to the supposition would be free from thorium, the atomic weight was determined by the sulphate method:—R_2O_3, 1·8929; $R_2(SO_4)_3$, 5·0674; R^{III}, 47·55. Thus the atomic weight had decreased by only 0·45 units, and the method was useless.

III. *Experiment to Separate Scandium and Thorium with Iodic Acid.* (Initial Material, 47·55).—The oxide obtained from the atomic weight determination described under II. was dissolved in dilute hydrochloric acid, some cc. of concentrated nitric acid were added, and then sufficient of a concentrated solution of iodic acid to give a precipitate. This consists essentially of thorium iodate. The filtrate was reduced with sulphurous acid, and the boiling solution was precipitated with ammonia. The hydroxide was carefully washed free from iodine with boiling water, dissolved in dilute hydrochloric acid, and the oxalate was precipitated from the solution, In the oxide obtained by the ignition of the oxalate the following atomic weight determination was carried out:—R_2O_3, 1·2220; $R_2(SO_4)_3$, 3·3221; R^{III}, 45·82. It will be seen that this is a very effectual method, for by one application of it the atomic weight of the material can be reduced from 47·55 to 45·82; *i.e.*, by 1·73 units. It is quite possible that the repeated application of the method would lead to the complete elimination of the thorium. But experiments in this direction were discontinued, because in the meantime we had found in the carbonate method described below a simpler and absolutely certain means of preparing larger quantities of scandium free from thorium.

IV. *Experiment to Separate Scandium and Thorium with Ammonium Sulphate.* (Initial Material, 47·55).—The fact that scandium potassium sulphate is difficultly soluble in a saturated potassium sulphate solution (Crookes, *Zeit. Anorg. Chem.*, 1909, lxi., 360), suggests that the corresponding ammonium salt would behave similarly, and as thorium ammonium sulphate is comparatively easily soluble a separation based upon this property seemed not impossible. But it was to be supposed that the complete separation of thorium could only be effected by repeated fractional precipitation. If ammonium sulphate in excess is added to the solution of a scandium salt made slightly acid with sulphuric acid, the double salt separates in crystals. The first fraction was used for the following atomic weight determination:—R_2O_3, 0·5245; $R_2(SO_4)_3$, 1·4171; R^{III}, 46·51. Thus the method seemed promising, but there would be a considerable loss of substance if it were carried out completely, so it was not further worked out.

V. *Experiment to Separate Scandium and Thorium by the Extraction of the Oxalate with Hydrochloric Acid.*—As thorium oxalate is the most insoluble in acids of all oxalates of the rare earths, while scandium oxalate, on the contrary, is relatively the most soluble in acids, it might be confidently expected that a fractional precipitation with oxalic acid, or a systematic extraction of the oxalate with hydrochloric acid, would lead comparatively easily to the separation of the two earths. As the first step in the investigation of this method, the solubility of scandium oxalate in hydrochloric acid of varying concentration was approximately determined at the boiling-point. It was then found that 10 per cent hydrochloric acid at the boiling-point dissolves 0·8, and 20 per cent 1·8 per cent of the oxalate. (Referred to the hydrated salt). Then 10 grms. of oxalate were subjected to a systematic extraction with 20 per cent hydrochloric acid, which was performed according to the well-known scheme of fractional crystallisation. Thus four series of fractions were formed. The spectrographic comparison of the oxides isolated from the most difficultly soluble part, and from the combined last liquors, showed that the latter were actually free from thorium; *i.e.*, that the extraction had led to the desired result. Thus all the thorium was concentrated in the difficultly soluble fractions. Nevertheless, the method does not seem suitable owing to its tediousness. Moreover, the yield of pure scandium is too small, and the fractional extraction must be continued for an exceedingly long time in order to collect most of the scandium free from thorium in the most soluble fractions.

VI. *Experiment to Separate Scandium and Thorium by Fractional Sublimation of the Anhydrous Chloride.*—In his famous prognosis of "Ekaboron" Mendeleeff (*Liebig's Ann.*, 1871, Suppl. 8, p. 198), on the basis of the periodic system, expressed the opinion that scandium chloride must be more volatile than the chlorides of the other rare earths. This is correct as regards the cerite and yttrium earths, but thorium chloride is one of the more volatile chlorides—it sublimes in a current of chlorine between 700° and 800° (R. J. Meyer and Gumperz, *Ber.*, 1905, xxxviii., 822; v. Wartenberg, *Zeit. f. Elektrochem.*, 1909, xv., 866)—so that a separation of scandium and thorium based upon this property does not at first sight appear possible. As the properties of anhydrous scandium chloride are not well known the following information may be given on the subject.

Anhydrous Scandium Chloride, $ScCl_3$.

The very simple and convenient method of Matignon and Bourion (*Comptes Rendus*, 1904, cxxxviii., 631) was used to prepare the compound; it depends upon the action of a current of chlorine charged with vapours of sulphur chloride on the oxide. The latter was heated in a Heraeus electric furnace in a glass or porcelain tube, the temperature being measured by means of a Le Chatelier pyrometer.

The decomposition of the oxide begins at about 500°, and is very soon completed. If the temperature is raised the chloride begins to sublime in fine transparent sparkling leaflets. The temperature of sublimation lies between 800° and 850, *i.e.*, *rather higher than that of thorium chloride.* The chloride is very strongly hygroscopic; it deliquesces rapidly in the air; in water it dissolves with hissing and generation of heat; the solution has a strongly acid reaction. It does not dissolve in absolutely anhydrous alcohol. When heated in the air it passes into an insoluble oxychloride which is stable towards acids and alkalis, even when heated with them.

Sublimation experiments with scandium containing thorium (R^{III} 48·0) were now carried out, the oxide being chlorinated in the usual way, and then a part of the chloride formed was sublimed at about 800°. The thorium chloride was thus completely transferred to the more volatile part. The two fractions were examined spectrographically. According to Prof. Eberhard the spectrogram of the residue was free from thorium lines, while the sublimate showed even the fainter thorium lines, and also traces of lead, calcium, aluminium, and silicon, probably derived from the porcelain.

The atomic weight of the less volatile thorium-free part was found by determining the proportion $R_2O_3 : 3C_2O_3$ in the oxalate.

Titration of the $KMnO_4$ *Solution; 2·903 grms.* $KMnO_4$ *per Litre.*

Oxalate used ..	0·3675	Sc_2O_3, per cent ..	32·27
Oxide by ignition	0·1186	C_2O_3, per cent ..	50·55
Cc. $KMnO_4$ used	28·80	R^{III}	44·94
C_2O_3 found . ..	0·1882		

It will be seen that the fractional sublimation of the chloride provides a very effectual method of separation. After one operation the atomic weight falls from 48 to 45. But the method cannot be used for working up larger quantities because it takes so much time, and from the nature of the method the yield of scandium free from thorium is unsatisfactory.

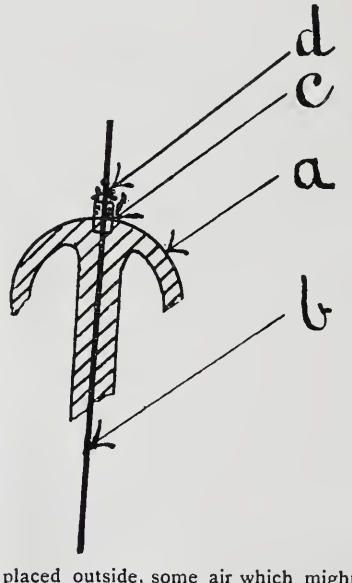
(To be continued).

Extraction of Germanium from Blende.—G. Urbain, M. Blondel, and M. Obiedoff.—The powdered blende is treated with its own weight of concentrated sulphuric acid and heated. The solid mass is taken up with water, and the insoluble residue is again treated similarly. Sodium sulphide is added to the aqueous solution, and the zinc is eliminated from the sulphides thus obtained by dissolving in sulphuric acid containing not less than 15 per cent of acid. The sulphides containing germanium are oxidised either with nitric acid or by heating in an oxidising atmosphere, the solution is evaporated to dryness, and sulphuric acid is again added. The solution is precipitated with sulphuretted hydrogen, and the sulphide precipitate is treated as before. If the germanium is not yet sufficiently concentrated the liquid is precipitated with ammonia and the precipitates are dissolved in sulphuric acid. The sulphides finally precipitated in hydrochloric acid solution are treated with ammonia in excess; the sulphides of germanium and arsenic containing traces of molybdenum instantly dissolve, and the solution is then cautiously precipitated with an acid which is more and more diluted as the process is continued. It is thus quite possible to precipitate all the arsenic and molybdenum, leaving the germanium in the solution, from which a perfectly white sulphide of germanium can be obtained.—*Comptes Rendus*, cl., No. 26.

VACUUM-TIGHT SEALS BETWEEN IRON AND GLASS.*

By HENRY J. S. SAND, Ph.D., D.Sc.

VACUUM-TIGHT seals for the introduction of metal wires into glass may be obtained by making use of the elasticity of small steel tubes which are employed as caps. The method of working is as follows:—An iron wire is sealed into the glass, and while the latter is still hot a small piece of heated steel tubing surrounding the wire is pushed a few mm. into the glass. After cooling, the steel tube is soldered to the wire. In the accompanying figure the cross-hatched portion *a* indicates the glass, *b* represents the wire, *c* the steel tube, and the dotted portion *d* the solder. The annular vacuum-tight seal is produced between the inner surface of the steel tube, which is expanded slightly and comes under tension, and the glass contained inside which is put under compression. Tubes into which iron wires of 1 mm. diameter have been sealed in this manner have been pumped out to a cathode-ray vacuum about four months ago, and have maintained their vacuum unchanged. In the earlier experiments the seal was usually arranged to be inside the evacuated tube, as it was thought probable that



if it were placed outside, some air which might possibly be trapped between the wire and the glass, would be difficult to remove completely by pumping. Latterly, however, cathode-ray tubes have also been made by a London firm of glass-blowers with these seals outside.

The fact that the seals will stand a certain amount of heating is proved by the circumstance that the soldering may be put on without damage.

It seems probable that seals between quartz-glass and iridium may be obtained in a similar way. This would be of value, as no method for introducing wires hermetically into quartz-glass is believed to be available at present.

Whether the seals will prove of technical importance for replacing platinum it is at present too early to say. It may here be pointed out that previous proposals to do away with platinum by the use of iron-nickel alloys or by using leads composed of thin flat strips of copper (Bastian, *Electrician*, 1907, lix., 230) have, so far as the author is aware, hitherto met with very little success. The author, however, believes that it should be possible to modify the present method of making seals in such a manner as to

* A Paper read before the British Association (Section A), Sheffield Meeting, 1910.

meet the requirements of rapid wholesale manufacture. It seems to him that the method should be free from the objection, which is often urged against the use of iron-nickel alloys, that they oxidise so much during working that the seals are not trustworthy, and also that the expansion coefficient of the alloys may not be relied upon to remain permanently unchanged. In the present case the thin steel caps may be heated in the flame so rapidly that there is no need whatever for more oxide to form than can be readily dissolved by the glass. The tubes also do not suffer from the disadvantage which may be urged against strips that they have edges along which a leak may be supposed to be capable of developing.

THE SERIES SPECTRUM OF THE MERCURY ARC.*

By S. R. MILNER, D.Sc.

With the arc in air there is always a continuous background to the spectrum present; this sets a limit to the faintness of the lines which can be observed, since attempts to photograph faint lines by increasing the time of exposure will simply result in the fogging of the plate by the background. The spectrum of the arc *in vacuo* is characterised by an almost entire absence of a continuous background, and exposures over 100 times the normal can be given before the background makes itself evident. Photographs of the mercury arc *in vacuo* with very long exposures showed many new lines, among which the lines forming the continuation of the various series of mercury were strikingly developed. The wave-lengths of the lines of the principal and of the diffuse series have been measured up to the fifteenth line, and those of the sharp series up to the thirteenth. The results afford a strict verification of Rydberg's law, that the frequency of the first line of the sharp series is equal to the difference of the limits of the sharp and the principal series.

ON THE ATTRACTION CONSTANT OF A MOLECULE OF A COMPOUND AND ITS CHEMICAL PROPERTIES.*

By R. D. KLEEMAN, D.Sc., B.A.

The writer has previously deduced from surface tension and latent heat data that the attraction between two molecules of the same kind is $\frac{K}{z^5}(\Sigma\sqrt{m_1})^2$, where z is the distance between the molecules, $\Sigma\sqrt{m_1}$ is the sum of the square roots of the atomic weights of the atoms of a molecule, and K is a quantity whose exact form is not known except that it has the same value for all substances at corresponding temperatures, and may therefore be a function of the distance between the molecules and the temperature. The quantity $\Sigma\sqrt{m_1}$ will be referred to as the attraction constant of the molecule. It was now pointed out that it can be shown strictly mathematically that the law of attraction cannot be completely determined from surface tension or latent heat data. The law deduced must contain an unknown function of the distance between the molecules and the temperature. It follows therefore that, if we assume a law of attraction between molecules, and deduce from it a formula for the surface tension or latent heat, and find that it fits the facts, it does not therefore follow that the law assumed is correct. In order to be on safe ground it is necessary that the law deduced should contain an unknown function. Now, this is the case with the law given above, the exact nature of K being not known. Further, since K is the same for all substances at corresponding temperatures, it does not contain $\Sigma\sqrt{m_1}$, and the chemical attraction of a molecule is therefore proportional to $\Sigma\sqrt{m_1}$, and this result should be true.

The attraction constant of the atoms of a molecule of a compound we would expect to be connected with its chemical properties. Thus it was found that the properties of the quantity $\frac{Tc}{\Sigma\sqrt{m_1}}$ of a substance, where Tc denotes the critical temperature, run parallel with its purely chemical properties. Thus the value of this quantity is constant for a compound and its substitution products, when an atom is replaced by an atom. Further, if we write $A - B = \frac{Tc}{\Sigma\sqrt{m_1}}$, where B denotes the chemical formula of a substance, the quantities for which B stands and the quantity A have the same values for a group of substances possessing similar chemical properties, but which vary from group to group. Thus, for example, in the case of the esters we would have $A-[2O+a(C+2H)]=\frac{Tc}{\Sigma\sqrt{m_1}}$, which may be written $A_1 - aB_1 = \frac{Tc}{\Sigma\sqrt{m_1}}$, where a denotes an integer. The values of A_1 and B_1 are found to be the same for each ester.

The various chemical compounds can be divided into groups in the above way; and it is found that this grouping coincides with that obtained from purely chemical considerations. The amines thus fall into three groups corresponding to the primary, secondary, and tertiary amines. The nitriles fall into a group, and so do also the ethers and the primary alcohols, and the secondary alcohols (omitting two alcohols which we know are, to a great extent, polymerised). The study of the quantity $\frac{Tc}{\Sigma\sqrt{m_1}}$ may therefore be of great assistance in the classification of the chemical compounds into groups, and to obtain various other connections between them.

* Abstract of a Paper read before the British Association (Section B)' Sheffield Meeting, 1910.

REPORT ON SOLUBILITY.*

By J. VARGAS EYRE.

The importance of the study of solubility is emphasised; the opinion being expressed that the time is not far distant when determinations of solubility as indicative of the reactivity or condition of saturation of substances will be more generally recognised.

From almost the earliest times to the present the solubility of substances has formed the subject of scientific inquiry, a vast amount of work has been recorded, and many conflicting opinions have been from time to time advanced.

In view of this state of affairs it was deemed desirable to classify all the published work of general and theoretical interest, not only to show the present position, but to indicate more clearly the direction future work on this subject should take.

The report submitted is the outcome of a systematic study of the literature bearing on the question of the solubility of substances in general; the material is classified chronologically and according to subject, and contains a brief statement of the main conclusions arrived at by the various authors.

* A Report presented to the British Association (Section B), Sheffield Meeting, 1910.

ON THE

NUMBER OF ELECTRONS IN THE ATOM.*

By J. A. CROWTHER, M.A.

THE experiments described were made to determine, by means of measurements on the scattering of β-rays, the number of electrons in the atom. Professor Sir J. J. Thomson has calculated the mean deflection ϕ experienced by a β-particle in passing through a thickness t of matter. It can be shown that—

$$\phi / \sqrt{t} = C,$$

where C is a constant depending only on the number of electrons in the atom, and known factors.

This relationship has been experimentally verified, and the value of $\phi / \sqrt{t}$ for several different elements determined. From these the number of electrons in the atoms of different elements has been calculated. It was found in every case that, within the limits of experimental error, the number of electrons in an atom was equal to three times the atomic weight.

ON THE NEGLECT OF SCIENCE IN COMMERCE AND INDUSTRY.†

By Sir WILLIAM A. TILDEN, F.R.S.

A DISCUSSION "On the Neglect of Science in Commerce and Industry" seems to involve the assumption that this neglect is general if not total. As this would be an exaggeration, I prefer to speak of the inadequate appreciation of science in the British commercial and industrial world. During the last thirty years immense efforts have been made to provide instruction in physical science for all classes in the community, and with some success. Every British university is provided with laboratories and gives degrees in science; the number of colleges and technical schools has increased enormously, and the quality of the teaching provided has greatly improved, while there are but few secondary schools which are not furnished with good laboratories in which physical science is taught up to a comparatively advanced stage. Out of these universities, colleges, and schools proceed annually many hundreds of young people with a tincture of scientific knowledge, some of them possessing even a certain amount of practical skill and experience. I do not refer to engineers whose training and professional qualifications require separate discussion.

Of this large number of scientifically educated persons the majority become teachers, while the minority only, roughly estimated at about one-third of the whole, find employment in connection with the arts and manufactures. It is the position of these persons which appears to be unsatisfactory, their knowledge and usefulness, their influence on the development of the industries, their pay and prospects being greatly inferior to those of the corresponding classes in Germany and Switzerland and in the United States. I can say nothing about France. This unsatisfactory state of things is, in my opinion, attributable to three causes, viz., the general ignorance of employers, the inefficiency of many of the men employed as chemists and electricians, and the bad example of the State. I will only venture to discuss these circumstances briefly.

1. Leaving out of account the small number of eminent scientific manufacturers and employers, such as the late Sir I. Lowthian Bell, Sir Bernard Samuelson, and Dr. Ludwig Mond, it is no exaggeration to say that a very large proportion of British chemical manufactures are carried on by men who have received no scientific training and are frequently ignorant of the principles involved in the processes of manufacture they conduct. Many boards of directors and many firms could be pointed out in which there is not one individual possessing adequate scientific knowledge. Such employers are wholly dependent on managers and foremen, paid servants, who may in some cases have a small interest in the concern, but who in any case are subordinate, and exercise small influence on the commercial policy or the development or improvement of the processes of manufacture. It is obvious that such employers work under great disadvantages compared with the man who is master of the principles, mechanical, chemical, or electrical, which underlie his processes, as well as being familiar with the technical operations which are carried on in his factory.

2. The inefficiency of many of the men who get employment in manufactures as chemist or electricians operates disadvantageously in two ways. Not only are their services of less value to their employers than they should be, but when this is recognised by the employer discredit is thrown on science, and the ignorant employer thinks it of no use. One consequence of this is that the sort of remuneration offered to young scientific men is commonly ridiculous. I will quote one instance only out of my own experience. I was asked by an influential member of a well-known firm (the name and business of which I must suppress) to recommend to him a young man who was to be such a good chemist and engineer that if anything went wrong in the works he would be competent to set it right, but he was also to be a person of such commercial experience and capacity as to be qualified to meet and deal with the business men of the great city in the near neighbourhood of which the works were situated. My reply was to the effect that it seemed to me that two men were wanted, but, anyway, I ventured to inquire what sort of terms and conditions would be offered to this combination of scientific attainment with commercial aptitude. I was informed that the salary offered was £75 for the first year, and, if the man engaged proved satisfactory, he might expect £150 the second year!

Such conditions as these are not calculated to attract young men of ability, and accordingly a very large proportion of those who find employment in industrial work are people of imperfect general education, with very doubtful qualifications as specialists, and the work they are competent to do is chiefly of a routine character, mere testing in fact; anything in the nature of experimental research being beyond their powers. This would be of less serious importance if their masters were able to direct the investigations which ought to be going on. But as they are incompetent to do this, and find their assistants in the same condition, the only result is distrust of science as the natural and indispensable source of industrial progress.

As to the absence of demand for scientific assistance or high character, I will only quote from a paper communicated to the International Congress of Applied Chemistry held in London last year. The author, Dr. E. F. Ehrhardt, a former student of mine, has been for many years on the scientific staff of the great Badische Fabrik at Ludwigshafen. He knows both England and Germany well and the industrial circumstances of both countries. This is what he says:—"The field for applied chemists in England is very restricted. I studied chemistry in England for three and a-half years at what is now the University of Birmingham, and then for two years in Munich. Of my contemporaries who studied chemistry with me in England, those who have found a living as industrial chemists in England could be counted on the fingers of one hand, whilst of my contemporaries in Germany nearly all are engaged in the industry."

Dr. Ehrhardt attributes the neglect of science by the British manufacturer to the unsatisfactory condition of the Patent Law in England. But though he is doubtless correct in his assertion that our patent law is inadequate, the existence and prosperity of a few chemical works in

* A Paper read before the British Association (Section B), Sheffield Meeting, 1910.

† Contribution to Discussion at the British Association (Joint Meeting Sections B and L), Sheffield Meeting, 1910.

this country, where good scientific control exists, shows that this inadequacy does not account for the general want of appreciation of science which prevails among British manufacturers. It looks rather like an indolent habit of mind engendered by previous generations of prosperity.

3. The indifference of British manufacturers toward science is consistent with the indifference of the State. It is not surprising that science plays but a small part in the affairs of the nation, while its absence is so conspicuous throughout the administrative offices of government. From the members of the Cabinet downward it would be difficult to find in Whitehall an official holding a superior administrative post who has received an education in which physical science formed any substantial part or who has made scientific principles a serious study. From time to time heroic speeches are made, but the measure of parliamentary sentiment in favour of science is to be found in the moderation of the grants to the modern university colleges, which are mainly scientific, and to the new Imperial College of Science and Technology, which has been founded with high aims but without corresponding endowment.

THERMIC REACTIONS *IN VACUO*.*

By FRANK E. WESTON, B.Sc., and H. RUSSELL ELLIS, B.Sc.

(Concluded from p. 161).

Part II.—*Experiments with Mixtures of Aluminium and Sodium Peroxide.*

Mixtures of Al powder and Na_2O_2 react vigorously and with great heat evolution in the air, when treated with a very small amount of water; this is especially the case with the mixture made in the proportion of $4Al$ to $3Na_2O_2$; one drop of water allowed to fall on a few grms. of this mixture produces a violent reaction, accompanied with a vivid flash of light. When such mixtures, however, are treated with water *in vacuo* no such reaction takes place, but only a slow evolution of gas is observed. In a partial vacuum it is found that the reaction takes place, but always then much quieter than in the air. The experiments described below were carried out on the mixture $4Al$ and $3Na_2O_2$. The apparatus used was similar to that described in Part I., Fig. 3, excepting that the leading wires were replaced by a tap funnel and the bottles varied from one-half to 1 litre in capacity. From 1 to 2 grms. of the mixture was used in each experiment, and was contained in a porcelain crucible.

Experiment 1.—Bottle charged and exhausted on water-pump till manometer read 720 mm.; barometer reading 750 mm. One drop of water produced a vigorous action; a flash of light, and the bottle smashed.

Experiment 2.—New bottle charged and fitted up, but on leaving for two minutes preparatory to exhausting, reaction took place with such violence as to blow out the cork.

Experiment 3.—Apparatus as Experiment 2; exhausted on water-pump and then on Töpler. One drop of water produced no reaction; more water (up to 10 drops), no reaction; air admitted, no reaction.

Experiment 4.—As in Experiment 3, but before exhausted on mercury-pump the mixture reacted with explosive violence as in Experiment 2.

Experiment 5. Clean, dry apparatus used and exhausted as in Experiment 3. No reaction produced by 3 drops of water, but on allowing air to enter till manometer stood at 500 mm., reaction started and went smoothly to an end; pressure reading at end of experiment was 450 mm. on manometer.

Experiment 6.—As in experiment 5. No reaction at first, but after a few minutes a vigorous evolution of gas took place, but no incandescence produced; reaction proceeded thus till manometer stood at 300 mm.

From these experiments and a few more of a similar nature not described, the following conclusions were arrived at:—

1. The apparatus must be perfectly dry and clean before charging with the mixture. The gases produced in the reaction—steam, H, &c.—must be completely removed before re-charging, otherwise the reaction starts apparently spontaneously. The sand must be removed and ignited before each experiment.

2. Only 1 drop of water is required to start the reaction in a normal manner, but more water prevents the normal reaction and causes a secondary one, which is probably as represented by the following equations:—

$$Na_2O_2 + H_2O = 2NaOH + O$$
$$3NaOH + Al = Na_3AlO_3 + 3H$$
$$H_2 + O = H_2O.$$

3. Reaction does not start in absolute *vacuo*, but the mixture becomes wet, whereas in air the first drop of water does not wet the mixture but causes the reaction; in dropping water rapidly from a burette into the mixture in air, the reaction takes place just as readily as if only one drop is used.

Further experiments were carried out in which great care was taken to have reacting bottle and materials perfectly dry and clean. The following are a few typical ones:—

Experiment 1.—Apparatus as in previous experiments; barometer, 743 mm.: manometer, 720 mm. Three drops of water added, no reaction except slight effervescence; pressure increased till manometer read 600 mm., and more water added but without effect. Pressure brought to atmospheric and crucible removed. The mixture was then covered with water, but no reaction took place. The water was poured off and the moist surface removed, and on adding one drop of water to the freshly-exposed dry surface the reaction immediately took place with the normal intensity.

Experiment 2.—Same as Experiment 1, only starting with manometer at 640 mm.; no reaction obtained. On removing crucible as in Experiment 1 the dry powder reacted instantly with one drop of water.

Experiment 3.—Same as experiment 2, but manometer at 500 mm.; reaction took place on addition of two drops of water; the manometer fell rapidly during the reaction, but finally rose to 510 mm., and then began to very slowly fall.

Experiment 4.—Same as previous, but manometer at 550 mm.; four drops of water started the reaction.

Experiment 5.—Same as previous, but a crucible lid used instead of a crucible, and the mixture was well spread out over the lid. Manometer at 550 mm.; reaction started easily, and manometer rose to 570 mm., and then very slowly fell.

Experiment 6.—As in Experiment 5. Manometer 650 mm.; no action except slight effervescence; air admitted till manometer was 570 mm., and a drop of water allowed to fall into a dry part of the powder; reaction took place immediately.

Experiment 7.—As in Experiment 6. Manometer 700 mm.; no reaction; reaction started when manometer was at 550 mm.

From a large number of similar experiments it was found that the reaction could be started when pressure in the apparatus was between 183 mm. and 193 mm.

Experiments on other fuses were tried, but it was found that the fuses either would not react at all in air with water, or else reacted with explosive violence. For example:—

1. A mixture of Mg and Na_2O_2 exploded when treated with two drops of water.

2. A mixture of $2Mg$ and Na_2O_2 gave no reaction with water except a quiet effervescence.

3. A mixture of $3Mg$ and Na_2O_2 behaved as in 2.

One or two drops of concentrated HCl, however, produced violent explosions with all the mixtures.

After many trials it was finally found that the best fuse to use *in vacuo* was a mixture of $4Al$ and $3Na_2O_2$, and that it could best be fired by an iron wire electrically heated.

* A Paper read before the Faraday Society, May 31, 1910.

Part III.—*Reduction by Magnesium Powder of Silicic Anhydride.*

Magnesium powder readily reduces silicic anhydride in presence of air without external heating during the reaction; the products consist of free silicon, one or more of the silicides of magnesium, magnesium oxide, and possibly silicon monoxide.

It has been shown previously that in similar actions the air plays an important part, more especially in the initial stages of the reduction. In the experiments now described the interaction has been studied in absence of air, and mixtures containing the following varying quantities of the constituents have been made to react *in vacuo* and the products examined.

Analysis of the Mixture resulting from the Reaction.

It was thought that by using excess of Mg it would be possible to use up the whole of the SiO_2, and by subsequent treatment of the residue with acids to obtain pure silicon. A mixture was therefore made consisting of equal parts of SiO_2 and Mg; for the reaction demanded by the equation $2Mg + SiO_2 = 2MgO + Si$, 48·7 parts Mg are required to 60 parts of SiO_2.

Twelve reductions were carried out, each time 20 to 30 grms. of the mixture being used; the contents of the crucible from each reaction were powdered, mixed, and analysed. The products consisted of free Mg, unreduced SiO_2, two or more silicides of Mg, free Si, MgO, and possibly some silicon monoxide.

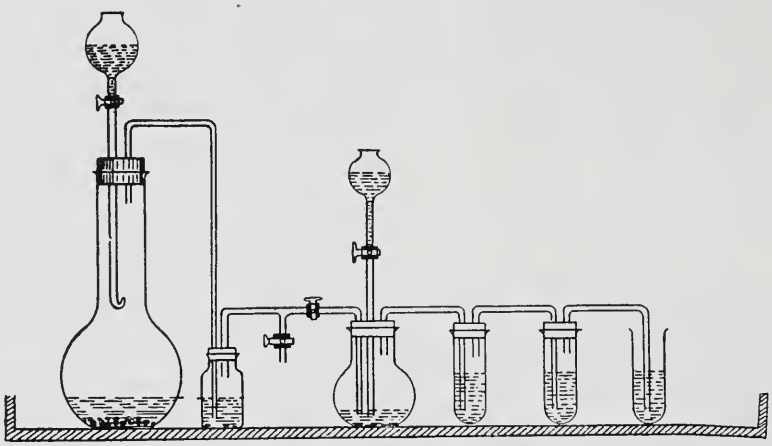


Fig. 4.

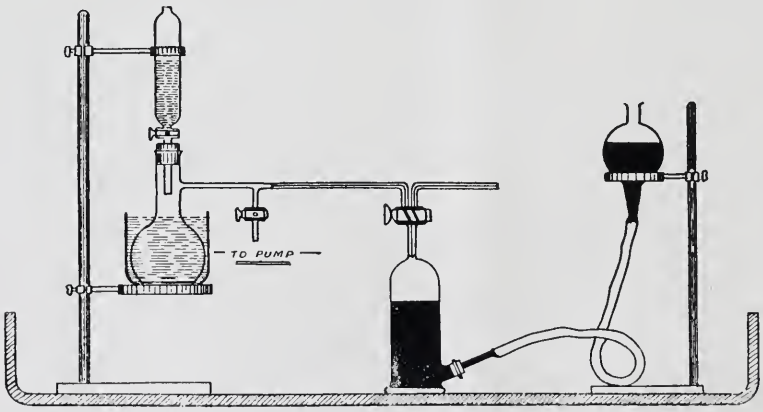


Fig. 5.

(*a*) Equal weights of each.
(*b*) In proportions $Mg + SiO_2$.
(*c*) In proportions $2Mg + SiO_2$.
(*d*) In proportions $4Mg + SiO_2$.

The magnesium powder was supplied by Kahlbaum, and was found to contain a small amount of $MgCO_3$, which caused an evolution of gas during the reduction.

The silica used was precipitated, and before use was strongly ignited.

The fuse used to start the reaction consisted of a mixture of Al powder and Na_2O_2 in proportion $4Al$ to $3Na_2O_2$.

The apparatus used was the large bottle of about 3 litres capacity, fitted up as shown in diagram 3, Part I.

The complete quantitative analysis of the mixture has not yet been successfully carried out, owing to the difficulties met with.

The authors are carrying out experiments to throw light on the formation of "monox," and to find certain reliable tests for this substance. Owing to lack of reliable information with regard to magnesium silicides, no complete estimation of these bodies has yet been made.

1. *Examination and Estimation of Silicides.*—On treatment with strong HCl a large amount of spontaneously inflammable gas was evolved, and on washing and drying the residue at 100° C. and then treating with HF more inflammable gas was evolved. It was found impossible to completely decompose the silicides with HCl; this was either due to (*a*) a protective layer of SiO_2 formed in the

reduction, (*b*) to a film of SiO_2 deposited during the action of the acid, (*c*) to different silicides being present which are unattacked by HCl.

The decomposition by HCl was carried out in an atmosphere of hydrogen or CO_2 and also *in vacuo*, and in each case a large amount of undecomposed silicide remained.

2. *Decomposition in* CO_2 *or* H.—The weighed powder was placed in the middle flask and just covered with water; H or CO_2 suitably washed was passed through the apparatus until the whole of the air was expelled; by adjusting the taps shown a very slow stream of gas was then driven through the apparatus during the experiment. Strong HCl was added very slowly, and a vigorous reaction took place, the evolved gases passing through the three test-tubes, which contained $AgNO_3$ solution.

The $AgNO_3$ solution in the first tube became black immediately, while if the operation was carefully carried out the solution in the last tube remained clear.

The flask was warmed when the reaction had become slow, and H or CO_2 passed until the whole of the SiH_4 was driven over. The deposited silver was dissolved in HNO_3 after filtering and washing, and estimated by standard NH_4CNS.

The mixture in the flask still contained undecomposed silicides.

If the reactions are—

$$(a)\ Mg_2Si + 4HCl = SiH_4 + 2MgCl_2,$$
$$(b)\ SiH_4 + 4AgNO_3 = Si + 4Ag + 4HNO_3,$$

then 108 grms Ag $\equiv$ to 19 grms. Mg_2Si.

In two estimations—

1 grm. mixture used and 5·9 cc. of 0·098 N. NH_4CNS.

1 grm. mixture used and 6·35 cc. of 0·098 N. NH_4CNS.

corresponding to about 1·2 per cent Mg_2Si.

The estimation in this manner was abandoned after many attempts.

3. *Reaction between* HCl *and the Mixture* in vacuo.—The gas was generated by adding concentrated HCl very slowly and carefully to the mixture after exhausting the apparatus (see Fig. 5); the gas evolved was finally driven over into a mercury gas holder by means of freshly boiled distilled water, and was stored out of contact with water.

The gas when first made was spontaneously inflammable, but after storing for some time it lost this power and consisted of almost pure hydrogen, giving no deposit of SiO_2 when burnt. (The mixture, after keeping for some time and decomposed *in vacuo*, gave no spontaneously inflammable gas with HCl, although with HF this was given off rapidly). The gas evolved was estimated as shown later.

The residue in the flask, although it showed no reaction on warming with HCl, readily evolved spontaneously inflammable gas with HF.

The authors were not able to estimate the total silicides by this method, but consider that at least two silicides were present.

Method of Analysing the Gas.

A small volume of about 10 cc. of the gas was transferred very slowly into an explosion pipette containing a known volume of pure oxygen.

As soon as a bubble of the gas came into the oxygen a sharp explosion took place and a cloud of SiO_2 was produced. This continued until the whole of the gas was transferred. A slight black deposit formed on the bulb, probably due to a small amount of the gas being decomposed by the high temperature of the explosion.

The diminution in volume was observed and the residual gas sparked, the volume again noted, and finally the gas was mixed with electrolytic gas and again sparked.

Knowing the volume of gas used and the contraction after explosion, and assuming that the gas consisted of SiH_4 and H_2 only, the amount of each can be calculated.

To illustrate the method of calculation an experiment is given fully.

2 grms. mixture used.

247·3 cc. gas at 19° C. and 760 mm.

Analysis of gas: 14·5 cc. of gas used and passed into 49·9 cc. of oxygen.

Contraction after mixing = 20 cc.

Further loss on mixing with electrolytic gas = 1·7.

Total loss of oxygen = 7·4 cc.

Equation representing reaction between the gases and oxygen is—

$$xSiH_4 + yH_2 + 2xO_2 + \frac{y}{2}O_2 = xSiO_2 + (2x+y)H_2O,$$

where x and y are volumes of SiH_4 and H_2.

$$\therefore x + y = 14{\cdot}5$$
$$\text{and } \left(2x + \frac{y}{2}\right) = 7{\cdot}4$$
$$\therefore x = 0{\cdot}1$$
$$\text{and } y = 14{\cdot}4$$

The total loss on explosion was 21·7 cc.

For above composition should be 21·9 cc.

A large number of analyses gave the same result, showing the gas to consist of almost pure H mixed with a very small quantity of hydride of silicon, and that, moreover, a very small quantity of this gas is sufficient to inflame the hydrogen when mixed with air or oxygen.

This analysis enables the percentage of free Mg to be found; this was 12·27.

The action of the gas on KOH was examined, but the changes in volume were too small to be measured, showing the existence of traces only of gases other than hydrogen.

Estimation of Total Silicon in the Mixture.

It was thought possible to estimate the Si and SiO_2 by (*a*) dissolving in boiling HCl and weighing the residue left; (*b*) dissolving the Si in KOH and weighing the SiO_2 left; (*c*) fusing with KOH and estimating the total silica.

Concordant results could not be obtained, and it was found that the finely divided SiO_2 dissolved freely in both HCl and KOH, and that any treatment to render SiO_2 insoluble would also convert some of the Si into SiO_2.

The total silicon was found correctly by fusing with KOH, &c.; it was always necessary to evaporate HCl solutions to dryness and ignite, as the finely divided silica readily dissolved.

Percentage Si found = 22·124.

Estimation of Free Si.

The mixture was first heated with concentrated HCl and then with HF for several days. The residue obtained completely combined with Cl gas, forming $SiCl_4$. The percentages of Si found by this method were concordant and equalled 12·75.

Result of Analyses.

1. Percentage of free Mg = 12·27.
2. Percentage of free Si = 12·75.
3. Percentage of total Si = 22·124.

Hence (22·124—12·75) = 9·374 per cent of Si is combined as SiO_2, SiO, and silicides.

New Tertiary Glycol.—A. Béhal.—The hydrogenation of terpineol in presence of reduced nickel yields a tertiary menthol which is not optically active. The action of sulphuric acid on the alcohol gives a menthene which can be characterised by transforming it into menthone by means of iodine and mercuric oxide and silver nitrate. Thus pinene can be converted into menthene by means of the following stages:—Pinene, terpineol, hydroterpineol, menthene Δ^1_8, menthene, menthone.—*Comptes Rendus*, cl., No. 26.

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,*

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, &c.

By PERCY H. WALKER.

(Continued from p. 159).

Inks.

Writing Inks.

Almost without exception all black inks suitable for record purposes are iron-tannin inks. The determinations of an analytical character which are of value are as follows:—

1. *Specific Gravity.*—Determine with a pyknometer at 15·5 C.

2. *Total Solids.*—Weigh 10 grms. of ink in a flat-bottomed platinum or porcelain dish, evaporate to dryness on the water-bath, and then heat in an oven at the temperature of boiling water for two hours; cool in a desiccator and weigh.

3. *Ash.*—Burn the residue from the determination of total solids at a low temperature, preferably in a muffle. In order to avoid loss by foaming the dish used should not be too small, not less than 50 cc. capacity.

4. *Iron.*—Transfer the ash to a small beaker and dissolve in 15 cc. of hydrochloric acid with the addition of stannous chloride at the temperature of the steam-bath; reduce by adding stannous chloride, drop by drop, to the hot solution until the colour is destroyed, and then add one or two drops in excess. Wash the reduced iron solution from the small beaker into a 600 cc. beaker and dilute to about 250 cc. with cold water, add all at once an excess of mercuric chloride, stir, allow to stand a minute, and titrate with standard potassium dichromate solution.

5. *Sulphuric Anhydride, SO_3.*—Determine both iron and sulphuric anhydride in the same sample. Place from 10 to 15 grms. of ink in a platinum dish, add 1 to 1·5 grms. of sodium carbonate previously dissolved in water, evaporate to dryness, ash, extract with water, add bromine water to the extract, boil, render acid with hydrochloric acid, boil off the bromine, and determine the sulphuric anhydride (SO_3) by precipitation with barium chloride. Dissolve the insoluble residue in hydrochloric acid and determine iron as described in the preceding section. Or, in case the small amount of platinum (which always goes into solution when iron oxide is dissolved by hydrochloric acid in platinum) causes trouble with the potassium dichromate method, add sulphuric acid, evaporate to fumes, dilute, reduce with zinc, and titrate with potassium permanganate.

6. *Keeping in Ink Wells.*—Allow the bottle of ink to stand perfectly still at room temperature for three days. Carefully remove the stopper without shaking the bottle, and draw out about 50 cc. with a pipette from the middle of the bottle. Filter this through a dry paper, exposing as little as possible to the air, and place 25 cc. of the filtrate in a clear glass bottle 140 mm. high and 56 mm. in diameter, with a neck 32 mm. in diameter (an 8-ounce salt-mouth bottle). Cover the top of the bottle with a piece of filter-paper, using a small amount of mucilage or paste to fasten the paper firmly across the neck. Let it stand at room temperature and in ordinary daylight in a room free from acid or ammonia fumes for fourteen days, observing from day to day whether mould or any film on the surface forms, and whether any sediment forms on the walls or bottom of the bottle.

7. *Action on Steel Pens.*—Immerse steel pens in the ink and leave them there for seven days. Remove the pens each day, clean them and note whether the metal appears corroded; also whether the ink has become thick.

8. *Streak Tests.*—Procure a supply of uniform good quality white all rag writing paper in sheets 265 × 200 mm. Stretch the paper on a smooth board inclined at an angle of 45° and let about 0·6 cc. of the ink flow from a tube held vertically near the top edge of the paper. For this purpose use a tube of approximately 3·5 mm. bore and 250 mm. in length, with a mark 62 mm. from the lower end. By drawing the ink up to the mark and allowing what will flow out to pass over the paper, uniform streaks can be made. Make streaks with the undiluted inks, and with the inks diluted with an equal volume of water. Allow to dry and cut into a number of strips.

9. *Penetration and Fluidity.*—The ink should penetrate into the fibres of the paper, but should not pass through it. This can be best observed on the streaks made for exposure tests. Stickiness should also be observed, and by carefully making the streaks and comparing a very good idea of the fluidity can be formed. A normal ink should give an oval head to the streak and the rest should be nearly uniform in width; a very fluid ink gives a wide head and rapidly narrows down.

10. *Resistance to Sunlight and Reagents.*—Cover half of some of the strips with black paper, clamp under glass in a photographic frame, and expose to sunlight. Expose other strips to the weather uncovered and keep some strips in diffused daylight in an atmosphere free from laboratory fumes for eight days. Use some of these last strips for the tests with reagents and preserve some for final comparisons. If the ink is a copying ink, make press copies of some of the strips as soon as they are thoroughly dry and treat the press copies and the copied original as in the other cases. In testing with reagents, immerse the strips in the reagents and observe the effect at the end of fifteen minutes, of one hour, and of twenty-four hours. Test, using the following reagents, though others may also be employed:—

Water; 95 per cent alcohol; 90 volumes of water and 10 volumes of ammonium hydroxide (0·90 sp. gr.); 90 volumes of 95 per cent alcohol and 10 volumes of ammonium hydroxide (0·90 sp. gr.); 2 per cent hydrochloric acid; 2 per cent sodium hydroxide; bleaching powder solution, N/200 available chlorine.

The tests used are relative, and it is well to have a standard ink for comparison. Such a standard may be prepared by the following formula:—23·4 gms. of pure dry tannic acid; 7·7 grms. of pure crystallised gallic acid; 30·0 grms. of pure crystallised ferrous sulphate; 10·0 grms. of gum-arabic; dilute hydrochloric acid in sufficient amount to contain 2·5 grms. of hydrochloric acid (25 grms. dilute hydrochloric acid U.S.P.), and 1·0 grm. of crystallised carbolic acid.

All of these chemicals should be of U.S.P. quality, and in addition the purity of the tannin should be determined by the hide powder method (U.S. Dept. Agr., Bureau of Chemistry, *Bull.* 107, Revised, p. 36).

Dissolve the tannin and gallic acid together in about 50 cc. of warm water, dissolve the ferrous sulphate in about 150 cc. of cold water, dissolve the gum-arabic in about 150 cc. of warm water. Allow the warm solutions to cool, add the hydrochloric acid to the ferrous sulphate, and immediately mix all the solutions and make up with distilled water to 1000 cc. Mix thoroughly and allow to stand for at least four days at room temperature. Without shaking the bottle draw out the ink to be used in making comparisons. This standard ink will not be of a good colour, but will make a dirty grey-green mark which will finally turn black. It may be coloured to match the ink under examination by addition of a small amount of soluble dyes.

11. *Rating.*—The rating of a number of samples of ink is entirely relative, and any system may be adopted. The exposure to sunlight is, of course, the most important test, and the following scheme answers very well for record inks. Rate the standard ink as follows:—

Exposure to sunlight	70
Exposure to reagents	10
Keeping quality, penetration, stickiness, fluidity, and action on steel pens	15
Composition	5
Total	100

* *Bulletin* No. 109, Revised, U.S. Department of Agriculture, Bureau of Chemistry.

Other record inks are given values above or below the figures for the standard ink, as the judgment of the analyst may indicate, so the total for a very good ink may be over 100.

Rate copying inks as record inks and make a separate rating on the copy, comparing one with another, and giving a weight of 50 per cent to clearness and depth of copy, and 50 per cent to resistance to reagents and sunlight. For further information consult Lunge ("Chemisch-Technische Untersuchungs Methoden," iii. 762), Schluttig and Neumann ("Die Eisengallustinten"), Mitchell and Hepworth ("Inks, Composition and Manufacture"), and Munson ("The Examination of Writing Inks," *Journ. Am. Chem. Soc.*, 1906, xxviii., 512). The chromate logwood inks and the vanadium inks are not permanent. Among the inks examined by Munson no sample with a specific gravity below 1·035 was permanent, and with one exception no sample containing less than 0·60 per cent of iron. The exception, however, was a very permanent ink, in spite of the fact that it contained only 0·32 per cent of iron.

Cancelling Inks having an Oil Base.

The work on Cancelling Inks is a revision of the methods previously issued as *Circular* 12 of this Bureau.

The following methods have been devised for the purpose of ascertaining the suitability of cancelling inks for the use of the Post-Office Department. Many of these methods will be found of assistance in passing upon the quality of stamping inks for miscellaneous uses. It is important that the ink used by the Post-Office Department for post-marking possess in the highest possible degree certain properties. The ink, first of all, must produce an indelible cancellation; that is, it must be relatively indelible as compared with the ink used for printing the postage stamps. The postmark made with the ink must dry quickly in order that the mail matter may be handled immediately without any blurring or smearing of the postmark. Both this property and the property of indelibility involve the question of the rate at which the ink penetrates or is absorbed by the fibre of the paper. A satisfactory ink does not harden or form a crust on the ink pad on exposure to the air. There must be no deposition of solid matter on the bottom of the vessel in which the ink is stored, and the pigments, on which the indelibility of the ink depends, if insoluble, must not settle out in such a way as to make it possible to pour off from the top of the container a portion of the ink which contains little or none of the insoluble pigment or pigments. The following methods have been found of value for the purpose of ascertaining the quality of a given sample of ink as well as the appropriateness of certain materials used for the manufacture of cancelling inks.

1. *Preparation and Care of the Sample.*—Since cancelling inks contain more or less insoluble and volatile matter, special attention must be given to the preparation and care of the sample. It must be carefully mixed by shaking before each portion is removed for analysis, and the container must be left open no more than is absolutely necessary for the removal of portions of the ink.

2. *Determination of Matter Volatile at Ordinary Temperatures.*—Place a carefully weighed quantity (between 5 and 5·2 grms.) of the ink in a flat-bottomed aluminium dish 102 mm. (4 inches) in diameter. Distribute the ink completely over the surface of the bottom of the dish by gently tilting the same. This quantity of ink should be sufficient to completely cover the bottom of the dish. Place the dish on a horizontal shelf or table where air will have free access to it and where it will be screened in such a way that no dust can fall into it. Re-weigh the dish at the end of eighteen hours, twenty-four hours, two days, three days, four days, five days, six days, seven days, fourteen days, twenty-one days, and twenty-eight days. Calculate the total percentage loss of weight at the end of each period of drying. The loss of weight should be gradual and should not exceed 15 per cent during the first seven days, nor 25 per cent during twenty-eight days. This test shows the absence of highly volatile ingredients and the absence of an excess of matter volatile at the ordinary room temperature. The constituents of a cancelling ink should be such that the volatile matter will not exceed the above limits when the ink is exposed under the conditions named to a summer temperature of 80° F. and upward.

3. *Determination of Relative Penetrating Power.*—(a) *Apparatus.*—(*a*) Homœopathic shell vials about 8 cm. long and 2—2·5 cm. in diameter. (*b*) Strips of white blotting-paper, which for a given series of determinations should be cut from the same sheet and of exactly the same dimensions. A convenient size is 12 mm. wide and 25 cm. long. (*c*) A pair of dividers with arms 15 cm. long or longer. (*d*) A millimetre rule.

(b) *Determination.*—Place approximately 5 cc. of the ink or other material to be tested in one of the "shell vials" described, and if several samples are to be tested arrange the vials in a row. Place 5 cc. portions of distilled water in each of two of the vials, and put one of the vials containing water at each end of the row of vials containing samples to be tested. Proceeding from left to right, insert a strip of blotting-paper in each of the vials, recording the exact time the paper was placed in each vial. The blotting-paper should maintain a nearly upright position. The liquids gradually ascend the strips by capillarity; the strips, however, should be in such a position that the liquid does not ascend by capillarity between the edges of the strips and the sides of the vials.

At the expiration of exactly fifteen minutes from the time each strip is inserted in the vial, measure the height to which the liquid has ascended the strip of paper by means of a pair of dividers and record the distance in millimetres. Make a second set of readings at the end of forty-five minutes.

After all of the measurements have been recorded reduce the results to the terms of the penetrating power of distilled water, taking the penetrating power of distilled water as 100. This is accomplished by dividing each result by the average of the results obtained for the distilled water contained in the vials and multiplying the quotient by 100. Ten samples may conveniently be tested at one time by working as described. The method gives good comparative results, and has been applied not only to cancelling and other stamping inks, but to the liquids used for the manufacture of these inks.

In observing the penetrating power of a given sample of ink it is important to remember that the value of a cancelling or stamping ink depends upon its power to penetrate the paper during the first minute or fraction of a minute following its application to the paper. It is well, however, to keep the tests under observation for several hours, as information can thus be obtained in regard to the extent to which the colouring matter contained in the ink follows the liquid base of the ink as it passes through the paper. In some cases the colouring matters keep pace with the liquid portions of the ink; in others an uncoloured band at the top of the portion of the paper which is wet with the ink shows that the colouring matter does not proceed through the paper as rapidly as the base of the ink. This may or may not be an undesirable result. If the colourless band is due to a difference in the rate of penetration, it is undesirable. If it shows that the dye contained in the ink has an affinity for the fibres of the paper, it is evidence of a valuable quality.

Additional information can be obtained from the penetration test by removing the strips of paper from the vials, cutting off the part of the paper which has actually been immersed in the ink, and treating the upper part successively with petroleum, ether, alcohol, and other solvents for removal of the constituents of the ink soluble in these liquids. The extent to which the dye or dyes contained in the ink resist the action of these solvents and the extent to which the lampblack has passed up the strip of blotting-paper are indices of the quality of the ink.

An examination of the strips with the microscope will give valuable information regarding the rise of carbon in

the paper and the affinity of the dye for the fibre of the paper. With many inks the carbon will not rise above the surface of the liquid, while with others it penetrates the paper to the same height as the dye. With this class of inks it is important that the base of the ink have the power to carry the carbon well into the fibres of the paper.

To make the determination allow the strips to remain in position until the next day, remove, dry between blotters, and examine for a rise of dye or carbon. If either dye or carbon rises as far, or nearly as far, as the base of the ink the rise is pronounced "satisfactory." Less than this is not acceptable except in the case of glycerin inks, which rarely give any rise of carbon. A small amount of rise in the latter inks must be accepted as satisfactory. To determine whether the rise is carbon or simply dye, pick off particles of the paper and adhering ink at intervals on the strip and mount on slides with water or alcohol. Examine with the microscope, using low power; note size of the carbon grains. The grains adhere to the outside of the paper fibres in clots, as a rule, but it is often difficult to distinguish them.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cli., No. 4, July 25, 1910.

Colour Assumed by Colourless Solutions of Coloured Substances when they Separate from Colourless Solvents.—D. Gernez.—Mercuric iodide which in its stable form is a magnificent red below 126° becomes yellow at higher temperatures, and it separates in the yellow variety, which is unstable below 126°, from its solutions even at low temperatures. Colourless solutions of mercuric iodide in paraffin, menthol, &c., when heated to 100° and then suddenly cooled, yield the yellow iodide, which changes colour, becoming orange and finally red.

Racemic Liquid Compounds.—A. Ladenburg.—The author has studied the fusion curves of inactive pipecolin containing varying amounts of *d*- and *l*-pipecolin. There is a eutectic point at −6·5° in a mixture containing 35 per cent of *l*-pipecolin, and the melting-point of racemic pipecolin (50 per cent *d*- and 5 per cent *l*-pipecolin) is −5°.

Place of Ultimate Rays in Spectral Series.—A. de Gramont.—Certain series of spectral rays occur, such that their wave-lengths are the terms of a series which may be calculated by formulæ containing two or three terms, of which one is a constant. The constants and the factors of the different terms are periodic functions of the atomic weights. Each of the series forms a group having common characteristics. The author has now studied the ultimate rays to see whether they fit into these series. For substances which possess a principal series the ultimate rays always belong to it. With substances for which no principal series has been detected the ultimate rays do not belong to the secondary series, but a characteristic doublet has been detected and considered as the first term of the principal series the following terms of which are still unknown.

Effect of Temperature and Pressure on Cyanogen.—E. Briner and A. Wroczynski.—High pressures induce the formation of para-cyanogen from cyanogen and also cause the decomposition of cyanogen into its elements. To produce an appreciable amount of para-cyanogen at the ordinary pressure the temperature must be raised to 310°.

Action of Ultra-violet Rays on some Carbohydrates.—Henri Bierry, Victor Henri, and Albert Ranc.—The authors have investigated the action of the ultra-violet rays on the sugars which generate certain polyoses (*e.g.*, saccharose, gentianose, raffinose, &c.). *d* Fructose undergoes a deep-seated decomposition, yielding formic aldehyde and carbon monoxide. This is the first case in which this sugar has been thus decomposed without the help either of ferments or chemical agents.

Aluminium Nitride.—Daffy Wolk.—Aluminium absorbs nitrogen at 820—850°. Below 700° the absorption is imperceptible. At 1000° it is rapid, while at 1100° dissociation occurs, and no definite product is obtained. The nitride which the author has prepared contains 33·6 per cent of nitrogen (34·06 for Al_2N_3). It is a grey amorphous mass, which is more easily decomposed by water the lower the temperature at which it was formed. Ammonia has no specific action on aluminium.

Decomposition of Water-vapour by the Brush Discharge.—Miroslaw Kernbaum.—When a brush discharge acts on water-vapour at the ordinary temperature, hydrogen peroxide and hydrogen are formed according to the equation $2H_2O \rightleftharpoons H_2O_2 + H_2$. The reaction appears to be an ionisation effect produced by the cathodic radiation, and it is probably not due to the influence of the ultra-violet light which accompanies the brush discharge.

Decomposition of Ether Oxides of Phenols by mixed Organo-magnesium Compounds.—V. Grignard.—When organo-magnesium compounds act on the ether oxides of phenol a complex oxonium compound is formed. Under the action of heat it splits up as follows:— $C_6H_5{>}O{<}^{C_2H_5}_{BrMg} = C_6H_5OMgBr + {}^{C_2H_5}_{C_5H_{11}}$. Apparently one atom of hydrogen then migrates from the one aliphatic radicle to the other, yielding a saturated and an ethylenic hydrocarbon.

Constitution of Vicianose.—Gabriel Bertrand and G. Weisweiller.—The hydrolysis of vicianose occurs according to the equation:—

$$C_{11}H_{20}O_{10} + H_2O = \underset{d\text{-glucose}}{C_6H_{12}O_6} + \underset{l\text{-arabinose.}}{C_5H_{10}O_5}$$

Vicianose is thus a disaccharide formed by the union of a molecule of *d*-glucose with a molecule of *l*-arabinose.

MISCELLANEOUS.

Second International Congress of Alimentary Hygiene.—The above Congress meets in Brussels from October 4 to 8, 1910. The following is the Provisional Programme:—

Tuesday, October 4.—10 a.m.: General Meeting in the "Palais des Fetes" of the Universal Exhibition. Lantern Lecture by M. Dastre, Professor à la Faculte des Sciences de Paris et Membre de l'Institut; Subject—"The Ultra-violet Rays and their Application to Alimentary Hygiene." 2 p.m.: Meetings of the Sections in the "Palais des Fetes." 5 p.m.: Lunch at "Le Chien Vert" (in the Exhibition).

Wednesday, October 5.—10 a.m. and 2 p.m.: Meetings of Sections. 4 p.m.: Lecture by M. Paterno, Vice-President of the Italian Senate, Professor of the University of Rome; Subject—"The Chemical Sciences." 7 p.m.: Banquet at the "Tavern Royale," Rue d'Arenberg.

Thursday, October 6.—10 a.m. and 2 p.m.: Meetings of Sections. 2 p.m.: Visits of Sections to the Exhibition. 4 p.m.: Lecture by M. Bordet, Director of the Pasteur Institute, Brussels; Subject—"Hygiene and Bacteriology."

Friday, October 7.—10 a.m. and 2 p.m.: Meetings of Sections. 7 p.m.: Gala Performance at the Theatre Royale de la Monnaie.

Saturday, October 8.—Morning: Visits to the Exhibition, to the Colonial Museum, and to the "Institut au Parc Leopold."

Members and Associates (subscription, 20 francs and 10 francs respectively) are admitted free to the Universal Exhibition during the time of the Congress. Special railway facilities have been arranged. Further information may be obtained of the Hon. Sec., CECIL H. CRIBB, 136, Shaftesbury Avenue, London, W.

THE CHEMICAL NEWS.

Vol. CII., No. 2654.

METALLIC RADIUM.

By Mdme. P. CURIE and A. DEBIERNE

To obtain metallic radium we used the methods described by M. Guntz for the preparation of metallic barium (*Comptes Rendus*, 1901—1905). Preliminary experiments were performed with very small quantities of material (about 0·1 grm.), which necessitated very careful work. The object of these experiments was to find out the best method of preparing radium.

The method was based upon the preparation of the amalgam and the expulsion of the mercury by distillation under suitable conditions. The amalgam was obtained by the electrolysis of a perfectly pure solution of radium chloride (atomic weight 226·5), using a mercury cathode and an anode of platinum-iridium. The amount of $RaCl_2$ was 0·106 grm., and that of the mercury about 10 grms. After the electrolysis the solution contained about 0·0085 grm. of salt. The amalgam decomposes water and alters very rapidly in the air. It was quite liquid, while in the same conditions we obtained a barium amalgam containing many crystals. The dried amalgam was rapidly transferred to an iron boat previously reduced by pure hydrogen. This boat was placed in a quartz tube, from which the air was then pumped out.

The distillation of the mercury is a very delicate operation; it must be performed without allowing the liquid to boil, otherwise some of the substance will be lost. It was finally carried out in pure hydrogen, the pressure of the gas being always greater than the pressure of saturated mercury vapour at the temperature of the boat. The temperature was determined by means of a thermoelectric couple, one soldered joint of which was connected with the metal of the boat. Owing to the small amount of material which we used we had to be particularly careful about the purity of the hydrogen; we found that hydrogen when purified and dried by the ordinary methods may still attack the amalgam and the metal. In order to get it quite pure the hydrogen was admitted into the apparatus through a platinum tube, which was heated to a high temperature in an electric furnace. This process produces perfectly pure hydrogen.

Most of the mercury was distilled at 270°; then the temperature was gradually raised as well as the gas pressure in the apparatus. In order to be able to watch the contents of the boat throughout the whole operation gas burners were used for heating. Towards 400° the amalgam was solid, but it fused as the temperature was raised and then mercury was liberated. The point of fusion could be determined very exactly, it gradually rose and reached 700°. At this temperature no further distillation of mercury was observed, and there was no condensation on the cold wall. On the contrary, the metal began to volatilise rapidly and the vapour attacked the quartz tube. The operation was then stopped. The boat contained a shining white metal which melted sharply at about 700°. We think that this metal is pure radium. It adhered strongly to the iron and could not easily be detached from it.

Metallic radium rapidly alters in air, becoming black, probably owing to the formation of a nitride. Some particles of the metal were detached by means of a little chisel; some of them when they fell upon white paper produced a blackening like a burn. When the detached metal is placed in contact with water it decomposes it energetically, and most of it dissolves, showing that the oxide is soluble. A blackish residue remains, which is almost entirely dissolved on the addition of a very little hydrochloric acid, and this residue must be the nitride resulting from the alteration of the metal in the air. Since dilute acid dissolves nearly the whole of the substance an appreciable amount of mercury cannot be present in the metal.

The boat with the rest of the metal was placed in a sealed exhausted tube in order that we might measure the penetrating radiation of the metal and ascertain whether it had the radio-active properties foretold theoretically.

Radio-active equilibrium has not yet been reached, but the first measurements show that the increase of activity agrees well with the law of the formation of the emanation and that the limiting radio-activity of the metal would be about normal.

Since metallic radium is much more volatile than barium, we propose to purify it by sublimation *in vacuo* on a cooled metal plate.—*Comptes Rendus*, cli., 523.

SCANDIUM.*

Part II.

By R. J. MEYER and HERBERT WINTER.

(Concluded from p. 165).

VII. *Final Separation of Scandium and Thorium by converting the Scandium into Scandium Sodium Carbonate.* (Worked out by M. Speter).—The experiments described under headings I. to VI. open up a series of possibilities for the separation of thorium from scandium, but they are not applicable as a method of preparation in the pure state, which is satisfactory from a technical and economical point of view. Such a "final operation" as regards simplicity of performance, certainty of success, and as far as possible avoidance of loss, should at least be not inferior to the methods used for preparing the raw substance, as they were described in the first article. We discovered a method answering to these requirements based upon an accidental observation. Scandium shares with thorium the property of giving compounds which are soluble in alkali carbonate, complexes being formed. If such solutions are sufficiently diluted with water and heated, in consequence of hydrolytic decomposition, basic carbonate or hydroxide separates, and at equivalent concentrations thorium is less basic than scandium. A further difference depends upon the solubility of the scandium and thorium carbonate complexes. When a solution of thorium sodium carbonate is boiled in a large excess of soda, finally an easily soluble double salt crystallises with the soda, it is decomposed by water in the cold. But when the same process is carried out on boiling a scandium sodium carbonate solution, a difficultly soluble crystalline scandium double salt separates at a concentration at which the thorium salt remains completely dissolved. This method led to a very effectual and convenient method of separation.

Scandium Sodium Carbonate, $Sc_2(CO_3).4Na_2CO_3.6H_2O$.

A nearly neutral solution of scandium chloride is poured into a hot soda solution containing 20 per cent of anhydrous sodium carbonate (1 litre of soda solution was used to 10 grms. Sc_2O_3). On stirring it all dissolves. It is then boiled over a naked flame, meanwhile stirring vigorously till the double salt separates. The liquor is decanted off while it is still hot, the crystals are boiled up a second time with fresh soda solution, and then washed on the filter disc with cold water, alcohol, and ether. The analyses gave:—

	Found I.	Found II.	Calculated for $Sc_2Na_6(CO_3)_7.6H_2O$
Sc.. ..	11·11	11·31	11·21
Na . ..	23·64	23·06	22·98
CO_3 ..	52·77	—	52·34
H_2O ..	12·48 (*a*)	13·86 (*a*)	13·47

(*a*) From the difference.

* *Zeit. Anorg. Chem.*, lxvii., 398.

In the same conditions a difficultly soluble ammonium double carbonate is formed, but its composition is very different from that of the sodium salt. The analyses agree very well with the unusual formula $2Sc_2(CO_3)_3.(NH_4)_2CO_3.6H_2O$. No potassium salt could be formed under the same conditions.

These double carbonates are much less soluble in cold concentrated alkali carbonate solution than in hot. This fact shows that at a lower temperature more easily soluble double salts, possibly containing more water, are stable. In cold water they dissolve completely without decomposition if with difficulty.

Even at greater dilution (about 2 per cent solution) the appearance of a turbidity, owing to hydrolytic decomposition, could be observed after standing for sixteen hours. Boiling decomposes the aqueous solution after a short time with separation of basic salt or hydroxide.

We shall now give detailed directions for the separation of thorium from scandium by means of the sodium double carbonate.

The solution of the chloride after evaporation on the water-bath is dissolved in a little water, and the concentrated solution is poured into soda solution. The latter must contain 20 per cent of anhydrous carbonate, and chemically pure soda must be used. One litre of soda solution must be used for 10 grms. of the worked up scandium oxide. By stirring and gently warming a clear solution is first obtained. It is heated till it boils vigorously, and kept boiling for half an hour. After boiling for a few minutes the double carbonate is deposited in crystals upon the bottom of the dish, causing violent spirting and bumping. For this reason it is convenient to use a mechanical stirring apparatus, which continually moves the crystals on the bottom of the dish. During the boiling the volume must be kept nearly constant by the addition of hot water. After a complete separation of the double carbonate has been effected by boiling for half an hour, the liquor is at once poured off from the heavy crystals, which have settled at the bottom, and the latter are boiled again three times with 20 per cent soda solution, each time for a quarter of an hour. The pure double carbonate thus obtained is dissolved by stirring it in a large quantity of cold water. The amount corresponding to 10 grms. dissolves in 2 litres of cold water, after stirring for about four hours. It is best to dissolve thus in water in order to separate off the impurities arising from the soda. The undissolved residue, which mostly contains an appreciable amount of iron, is filtered off. The clear solution is saturated with hydrochloric acid, the hydroxide is precipitated with ammonia while boiling, and the precipitate is washed very carefully with boiling water till it is quite free from alkali. This stage is reached much more quickly if the hydroxide is dissolved once more and again precipitated with ammonia. (The complete removal of the alkali is important, because in the subsequent oxalate precipitation, if even small amounts of sodium are present in the solution, an oxalate containiug alkali is always precipitated). The hydroxide is rinsed off the filter, and dissolved by boiling with as little dilute hydrochloric acid as possible ; then the filtered solution is precipitated with pure sublimed oxalic acid, and the oxalate ignited to oxide.

When this method of purification is used all the thorium remains dissolved in the filtrate from the double carbonate which separates, and can be detected with certainty in it by acidifying it and precipitating as oxalate. As regards the degree of purity of the scandium obtained from the double carbonate, even after once applying the process, the thorium is completely, or very nearly completely, eliminated. This may be shown by the examination of the oxide by physical methods :—

1. *The feeble radio-activity of scandium preparations containing thorium quite disappears after one purification with soda ; thus scandium earth is not radio-active.* (Dr. W. Marckwald kindly proved this by testing with an electroscope).

2. *The examination of the arc spectrogram by Dr. G. Eberhard showed that in the scandium oxide purified by soda no foreign lines were present, and in particular "in spite of the strongest illumination" thorium lines could not be detected.*

These proofs show that the preparations purified in this way—supposing that scandium is an element—are chemically pure products.

The material thus obtained, which had all the characteristics of a chemically pure substance, was now used for a very careful study of the atomic weight of scandium. But as this part of our work, which will be described in a special article, is not yet quite completed, we shall briefly give here only the provisional results, without going into the methods used in the determinations.

The three principal steps in the purification to which all the preparations used for the atomic weight determinations were subjected were the following :—

1. Precipitation with sodium silicofluoride.
2. Two precipitations with sodium thiosulphate.
3. Two conversions into the sodium double carbonate.

The determinations were performed partly by the analysis of the sulphate and partly by that of the oxalate.

I.

Series I. $R_2(SO_4)_3 : R_2O_3$.—Mean of five determinations (45·15—45·37) .. .. 45·22
Series II. $3C_2O_3 : R_2O_3$.—Mean of four determinations (44·94—45·33) .. .. 45·15

II.—*New Initial Material.*

Series III. $R_2(SO_4)_3 : R_2O_3$.—Mean of five determinations (45·06—45·34) .. .. 45·17
Series IV. $3C_2O_3 : R_2O_3$.—Mean of four determinations (44·86—45·16) .. .. 45·05

The soda method of purification was now applied once to this scandium, which had an average atomic weight of 45·15, but no further alteration was effected ; the atomic weight was again found to be 45·12.

Thus by the repeated application of the soda method a limit is reached, at which the atomic weight is 45.

It seemed desirable to check this result by the application of a new method which differed in principle from the methods employed.

In the separation of the rare earths usually those methods have proved specially effective which depend upon the fractional crystallisation of mixtures. The problem was therefore to find a scandium salt the properties of which—especially as regards solubility and power of crystallisation—would suggest the possibility of applying it for this purpose. But of all the known compounds of scandium none is suitable for this purpose, because some of them are too easily soluble, some are insoluble, and some are too easily split up hydrolytically. It occurred to us that the double nitrates frequently used for the separation of the cerite earths might be used for fractional crystallisation. But experiments in this direction showed that such double salts of scandium are not stable either in acid nor in neutral solution. On crystallising together scandium nitrate and alkali nitrate the components are obtained unchanged. Urbain (*Bull. Soc. Chim.*, 1896, [3], xv., 347) was the first to show that the rare earths form well crystallised stable salts with acetyl acetone, and these can be re-crystallised without undergoing decomposition. Thus thorium acetyl acetonate can be successfully used for fractional crystallisation. More information was given about these compounds by Biltz (*Liebig's Ann.*, 1904, ccci., 334) ; W. Biltz and Clinch, *Zeit. Anorg. Chem.*, 1904, xl., 218 ; all the literature on acetyl acetonate is given here).

Scandium also very easily gives a quantitative yield of a stable easily crystallising acetyl acetonate. It is precipitated in an amorphous form if acetyl acetone is added to a neutral solution of a scandium salt, and the free acid formed is neutralised with ammonia.

We shall now describe in detail the method of preparing the salt. Ten grms. of scandium oxide are dissolved in hydrochloric acid. The solution is evaporated to dryness on the water-bath, and the residue is taken up with 250 cc. of water. Forty-five grms. of acetyl acetone, dissolved in 32 cc. of concentrated ammonia (25 per cent) are added in the cold. The acetyl acetonate separates in the form of a flocculent voluminous white precipitate. After draining it off and drying on clay, the yield is 62 grms., while the theoretical yield is 50 grms, Thus the acetyl acetonate precipitated from aqueous solution contains water. The raw product is re-crystallised from dilute alcohol containing 71 per cent by weight. On cooling the solution the acetyl acetonate separates in large sparkling prisms. The salt is readily soluble in absolute alcohol, ether, and chloroform. It is insoluble in water. It melts between 187° and 190°. A determination of scandium gave :—

2·999 grms. acetyl acetonate gave 0·6062 grm. Sc_2O_3 = 13·14 per cent Sc.

Calculated for $Sc(CH_3COCHCOCH_3)_3$ = 13·18 per cent Sc. (Calculated for Sc = 45·1. For Sc = 44·1 the theoretical percentage of scandium in the acetyl acetonate would be 12·92).

The acetyl acetonate is volatile at a fairly low temperature and sublimes easily. The determination of scandium cannot therefore be performed by directly igniting the substance. For this purpose it must be decomposed with very dilute sulphuric acid, the sulphate being afterwards ignited to oxide.

On re-crystallising from dilute alcohol crystals are often obtained which are not quite anhydrous. Even on re-crystallising from absolute alcohol water remains in combination, and it can only be completely removed by crystallising from anhydrous ether. Finally, it must be mentioned that the acetyl acetonate has a tendency to undergo hydrolysis, giving basic products. These are detected by the appearance of a turbidity on boiling with dilute alcohol. Their formation may be avoided by previously adding some drops of acetyl acetone to the alcohol.

Acetyl Acetonate Fractionation.

By preliminary experiments it was first of all found that on fractional crystallisation of scandium acetyl acetonate from dilute alcohol, the impurities—yttrium earths and thorium—are rapidly concentrated in the final liquors. The atomic weight of the initial material was 48·1. After the formation of four series of crystals the slightly soluble fraction and the combined final liquors were tested. In the latter, thorium could easily be detected by the iodic acid reaction; similarly, the spectrographic examination of the oxide obtained from the final liquors showed the lines of thorium strongly, and those of yttrium and ytterbium faintly. It was afterwards found more convenient, instead of purifying the acetyl acetonate by systematic fractionation, to purify simply by repeated crystallisation from alcohol, as this simpler method is equally effective and leads more quickly to the desired result, besides entailing less loss of substance. The most difficultly soluble fraction obtained from the fractionation was used for the atomic weight determination, and the value it gave was R^{III} = 45·07. This number agrees very closely with the atomic weight of the products purified by the soda method. But in this case also it appeared doubtful whether, by the exhaustive application of the acetyl acetone process, the atomic weight could not be further lowered. For this reason 15 grms. of scandium oxide, R^{III} = 45, were converted into acetyl acetonate, and re-crystallised six times from 71 per cent alcohol. The concentration of the solution was chosen so that, on cooling the boiling solution, about 90 per cent of the salt separated. (In 100 cc. of alcohol, 71 per cent by weight, about 13 grms. of scandium acetyl acetonate dissolve on boiling). The solution was carried out with a reflex condenser, some drops of acetyl acetone being added. The liquors were evaporated on the water-bath till crystals again separated. The filtrates of these second fractions were put together as final liquors. The sixth lot of crystals were finally once more re-crystallised from *absolute* alcohol and then from absolute ether. They formed snow-white glittering needle-shaped crystals, which were used for the atomic weight determinations. The result was R^{III} = 44·90.

Thus the atomic weight had remained practically the same as before the re-crystallisation, which proves that no further removal af foreign substances had occurred. Moreover, the spectrogram of the re-crystallised product, according to Prof. Eberhard, was absolutely identical with that of the initial material, and also that of the oxide isolated from the combined final liquors showed no variation in the arc spectrum. No lines of any other known substance were indicated in it, so that *the scandium obtained from the acetyl acetonate purification must be regarded as pure, as well as that obtained from the carbonate method of purification.*

The above atomic weight determinations gave for the atomic weight of scandium a number closely approximating to 45·0, while Nilson, from the synthesis of the sulphate in four very concordant determinations, found 44·0. If O = 16 the value becomes 44·1. This number has been adopted in the International Atomic Weight Table, but it is doubtful whether it actually gives the true atomic weight of scandium. The chief doubt about its accuracy is due to the imperfection of Nilson's method. He gave only very indefinite information as to the conditions under which he made his scandium sulphate "neutral." Thus, he heated "to such a temperature that the sulphate formed was soluble in water," or, as he stated in another place, "so that only free sulphuric acid volatilised." But evidently it is necessary to know exactly the temperature of decomposition of the neutral and acid sulphates in order to hit exactly upon the point of neutrality. It is questionable whether Nilson in his purely empirical method actually obtained a neutral sulphate. How difficult it is to get this condition with the sulphates of the rare earths has been pointed out by Brauner and Pavlicek (*Proc. Chem. Soc.*, 1901, xvii., 63; *Journ. Chem. Soc.*, 1902, lxxxi., 1243). We have directed special attention to this point in a study of the atomic weight of scandium, which we have not yet concluded. Although we could to a certain extent estimate the value of the experiments which had been performed for the determinations described in the above article, we cannot say with certainty that the atomic weight one unit higher (45) is actually correct, and all the less because in some cases we have obtained values which are lower and different from the majority of the results without being able to detect the reasons for this deviation. It is possible, of course, that scandium from wolframite contains small amounts of an unknown substance. According to Prof. Eberhard this is suggested by some irregularities which appear in the arc spectrum. We hope soon to be able to communicate a complete explanation of these relations. This will be all the easier for us because Sir William Crookes has had the kindness to send us a specimum of the scandium oxide prepared by him from wiikite. By comparing with ours this preparation obtained from quite different initial material and by a different method, we shall be able to obtain a conclusive result from the atomic weight of scandium.

Electrolytic Preparation of Rubidium.—G. von Hevesy.—Metallic rubidium can be prepared by the electrolysis of the fused hydroxide by Lorenz's method—using a cathodic magnesite diaphragm—if the anode is also surrounded by a magnesite cylinder. The yield amounts to 30 per cent. The chief cause of the loss of current during the electrolysis is the conduction of oxygen by the melt. Contributory causes are the solution of the metal in the melt, and the occurrence of the reaction $RbOH + Rb \rightleftarrows Rb_2O + \frac{1}{2}H_2$.—*Zeit. Anorg. Chem.*, lxvii., No. 2.

THE MOLECULAR VOLUMES OF SOLIDS.

By H. H. STEPHENSON.

THE atomic volumes of the elements are a periodic function of their atomic weight, and Lothar Meyer's well-known curve is one of the most striking examples of periodicity, but our knowledge of molecular volumes is less satisfactory. Kopp and others have demonstrated that organic liquids near their boiling-point possess molecular volumes showing additive relations if certain arbitrary figures be taken for the atomic volumes of carbon, hydrogen, &c. Unfortunately, these arbitrary figures differ materially from the atomic volumes of the elements in the free state, and, further, their application to inorganic liquids leads to serious discrepancies.

However, we are not concerned in the present paper to challenge these conclusions as long as it is understood that such figures as 11 for carbon and 5·5 for hydrogen refer only to those elements when acting together in organic compounds.

Of the molecular volumes of solids practically nothing is known, and the literature of the subjeet is meagre and inconclusive. Text-books state that where compounds are chemically similar and isomorphous there is agreement in molecular volume, thus :—

	Specific gravity.	Molecular volume.
$MgSO_4.7H_2O$	1·685	146·0
$ZnSO_4.7H_2O$	1·853	146·9
$NiSO_4.7H_2O$	1·931	145·6
$CoSO_4.7H_2O$	1·924	146·0
$FeSO_4.7H_2O$	1·884	147·5

Considering that the group—$SO_4.7H_2O$—common to the above compounds averages four-fifths of the molecular weight, and that the metals concerned are very similar in atomic volume, it would be strange if the molecular volumes did not approximate. But other and quite dissimilar compounds can be found with molecular volumes equal to those given above, *e.g.*, $Ce_2(SO_4)_3$, 146; $(NH_4)_2SnCl_6$, 146; $Co(C_2H_3O_2)_2.4H_2O$, 147; $NiSiF_6.6H_2O$, 146. On the other hand, $MnSO_4.7H_2O$, which is chemically similar to, and isomorphous with, the given series, has a molecular volume of only 133. The following anhydrous sulphates of the type $R_2(SO_4)_3$ have very dissimilar molecular volumes :—Ce, 145; Sc, 147; Gd, 147; In, 151; Pr, 153; La, 159; Er, 173; Yb, 175. So that no generalisation can legitimately be founded on equality of molecular volume. It is to be feared that this erroneous impression has had a subconscious influence on chemists who thought that the densities they were determining should fall into line with some series such as that given above. We shall return to this matter later, when an explanation may be forthcoming both of the equality of molecular volume in one case and the inequality in the other.

In considering molecular volume, we must bear in mind the periodic character of atomic volume. If some acid radicle such as SO_4 be united to the element, the volume curve will, of course, be flatter, and will tend more to a straight line the greater the volume of the acid radicle, especially as the elements with low atomic volumes have higher valency than the others, but there is no ground for assuming that some law exists demanding equality of molecular volume.

It behoves us therefore to start afresh with no other prepossession but the periodic character of the atomic volumes of the elements. We must remember also that crystalline structure, water of combination, coefficient of expansion, and distance from melting-point, all have their influence on specific gravity, and the data of the greater part of them have not been determined; so that we must be content at first to lay down a few general rules of which the criterion will be their accuracy in forecasting specific gravities at present unknown, even perhaps of salts that have never yet been prepared. But no material progress can be made until the International Committee of Atomic Weights extends its functions to include all the physical constants of Nature.

The first point that meets us in the study of the molecular volumes of solids is that most of them are not the sum of the atomic volumes of the constituent elements as given in Lothar Meyer's curve. It becomes of importance, therefore, to ascertain what condensation has taken place, and for convenience we will reduce this condensation to percentages. If A be the sum of the atomic volumes, B the molecular volume, and C the percentage molecular condensation, then by definition $C = 100\,\frac{(A-B)}{A}$.

The oxides of the first group of the Periodic Table yield the following figures, taking the atomic values from the Meyer curve, liquid oxygen being 14·3 :—

Oxide.	Mol.Wt.	Sp. Gr.	Mol. Vol.	A.V.	C.
Li_2O . ..	30·0	2·10	14	40·5	66
Na_2O ..	62	2·25	27·6	61·7	55
K_2O.. ..	94·2	2·32	41	108·3	62
Rb_2O . ..	186·9	3·72	50	124	59
Cs_2O . ..	281·6	4·78	59	155	62

The condensations are remarkably similar, so that it is worth while proceeding to the second group.

BeO.. ..	25·1	3·02	8·3	19·2	57
MgO . ..	40·3	3·22	12·5	28·6	56
CaO.. ..	56·1	3·15	18	42·6	58
SrO	103·6	4·75	22	47·8	52
BaO.. ..	153·4	5·74	26·5	51	52·5

Again, the condensations are practically equal, though different from that of the first group. The sub-groups, also, have their own condensation.

Cu_2O . ..	143·1	5·75	25	28·5	12
Ag_2O ..	231·8	7·52	31	34·7	11
Au_2O . ..		?	?	—	?
ZnO . ..	81·4	5·48	15	23·5	36·5
CdO.. ..	128·4	7·30	17·5	27·3	36
HgO . ..	216	11·29	19·2	29	34
Hg_2O ..	416	10·29	39	43·7	11

It will be noticed that mercurous oxide falls into line with monovalent copper and silver of the first group. As the calculation of molecular condensation is quite simple, there is no need to detail all the figures of the other groups. The molecular weights are known, and the densities can be found from the molecular volumes given below with the condensations. Group III. of the Periodic Table is : —

Oxide.	M.V.	C.
B_2O_3	38·5	26
Al_2O_3	27·3	58
Ga_2O_3	?	?
In_2O_3	39	48
Er_2O_3	44·5	61
Sc_2O_3	35	48
Yt_2O_3	45	50
La_2O_3	50·2	43
Tl_2O	82	—

Boron is quite out of place, and so is thallium, but it will be found later that thallium falls in with the silver sub-group, while boron, the first element of this group, resembles carbon, and the other first elements of the following groups in showing a low condensation. The tendency of these elements is to form liquid or gaseous compounds which do not show any condensation at all.

Group IV.

Oxide.	M.V.	C.
SiO_2	22·8	46
GeO_2	22·5	46·5
SnO_2	23	47
(SnO	22·5	36)
PbO_2	27	43
(Pb_2O	45	11)
TiO_2	21·5	51
ZrO_2	24	49
CeO_2	25·3	48
ThO_2	27	46

Divalent tin agrees with the zinc group, and monovalent lead with the silver group.

Group V.

N_2O_5	66	38
P_2O_5	60	40
P_2O_4	50	41
As_2O_5	58	42
Sb_2O_5	85	22
Bi_2O_5	72	37
V_2O_2	37	41
V_2O_5	52	41
Nb_2O_5	59	40
Pr_2O_5	?	—
Yb_2O_5	?	—
Ta_2O_5	57	41

Antimony pentoxide is quite out of place, and one is inclined to suspect the density attributed to it is really that of the hydroxide. Tha other oxides of this group are :—

N_2O_3	53	32
NO_2	31	33
P_2O_3	51·5	27
As_2O_3	54	32
Sb_2O_3	53	32
Br_2O_3	58	32
V_2O_3	32	46
Nb_2O_3	?	?
Pr_2O_3	48	49
Yb_2O_3	43	—
Ta_2O_3	?	—

Group VI.

SeO_2	28	40
TeO_2	28·3	42
Cr_2O_3	30	48
MoO_2	19·8	50
WO_2	18	53
VO_2	24·5	41

Practically all the sesquioxides of the rare earths outside the third group have a condensation of 48, which is that of the scandium sub-groups. In Group VII. iodine pentoxide has a condensation of 40 like the pentoxides of the fifth group. The transition elements are :—

Mn_2O_3	35	41
Fe_2O_3	31·5	48
Co_2O_3	30	40
Ni_2O_3	34·3	40
Sm_2O_3	42	49
MnO	14	35
FeO	?	?
CoO	13	38
NiO	11·5	45

The monoxides of these elements gradually rise in condensation from manganese, which has the same condensation as the zinc group to nickel, which tends more to the lime group, assuming that its density is correct.

Such are the molecular volumes and condensations of the oxides of the elements, and it will be seen that in each group or sub-group condensation is equal, but that it varies with the groups, being greatest in the sodium group and least in the silver sub-group. As the sub-groups decrease in condensation, going from right to left in the Periodic Table, it seems probable that Group O, consisting of argon and its relatives, would have no condensation if it did form any oxides, which is equivalent to saying that the oxides would not be solids at ordinary temperatures.

Molecular condensation affords a valuable indication of the valency of a metal. Thus copper, mercury, thallium, iron, nickel, manganese, tin, and lead have different condensations in their *ous* salts from their *ic* salts, and it may be assumed that there is an actual change of valency. On the other hand, the oxides of rubidium and cæsium, Rb_2O, Rb_2O_2, Rb_2O_3, Cs_2O, Cs_2O_2, Cs_2O_3, Cs_2O_4, have all a condensation of 60, which may be explained by supposing that these represent different stages of oxidation, the metals remaining monovalent. Similarly, phosphorus is trivalent in P_4O_6, but pentavalent in P_2O_5 and P_2O_4. The same condensation occurs in NbO and Nb_2O_5, in TeO_2 and TeO_3, and in V_2O_2 in V_2O_5 respectively.

Before proceeding to a consideration of metallic salts, it is necessary to study the influence of water of combination and of crystalline structure on molecular volumes. The reader is by now aware of the thesis set out in this paper, viz., that condensation is the same in each group for any particular class of compound such as oxide or sulphate.

Crystallisation.

As might be expected, the molecular forces of which crystalline structure is the outward and visible symbol influence the density, and therefore the volume of a solid. Difference in form may alter the density of a compound by nearly 20 per cent. Amorphous arsenic, for example, has a density of 4·72, while the grey rhombohedra are 5·73. Again, lead monoxide is 8·74 in its hexagonal form, 9·37 as rhombic crystals, and 9·5 in the amorphous variety. In attempting to ascertain the order of specific gravity of the crystalline systems, where solids are polymorphous, we are faced with several exceptions, but a few general rules may be laid down. A mineral substance is practically always heavier than the artificially prepared substance. Richards and his associates have shown that atomic volumes vary under pressure, which makes the worker in this field doubly handicapped. He has comparatively few densities at his command, and many of those he has are suspect, as they pertain to minerals which may have been formed under pressure. Then, again, a crystalline variety is usually heavier than the amorphous substance. Exceptions are: —Yellow amorphous sulphur is denser than monoclinic, amorphous arsenious oxide than the regular octahedra, and amorphous lead monoxide than the hexagonal—assuming always that the densities given are correct. With many exceptions, the crystalline systems appear to be something as follows in order of density:—Tetragonal and rhombic, hexagonal, regular and triclinic, monoclinic, amorphous. But the chief fact about crystalline structure is that it may vary density, and therefore molecular volume, by nearly 20 per cent.

Water of Combination.

If RX be a solid compound of molecular volume v forming a hydrated variety RX, a H_2O of volume v_1, then $\frac{v_1 - v}{a}$ represents the volume of each molecule of water, modified by any change of crystalline structure that may have taken place. Kopp said the value for H_2O was constant at 12·4, but the average of over a hundred such cases gives water of combination a molecular volume of 14, the extremes being 8 and 18. So that calculations on the assumption that $H_2O = 14$ might be seriously inaccurate but for the fact that the variations occur generally when only 1 or 2 molecules of water are present. Salts that lose their water or part of it at little above normal temperature do not conform at all to the average. Thus the molecule

of water representing the difference between tellurous acid and its anhydride has a volume of 31, but the water is lost at 40° C. This is on a par with the abnormal condensations of anhydrous compounds which melt under 100° C. For the purpose of this paper, a solid must be defined as one remaining solid at the boiling-point of water.

There seems to be no indication of definite influence on the molecular volume of water by the various crystalline systems. Extremes are met in each class, but the more numerous the examples of any class the more it tends to the average 14. As the densities of many salts are only given for their hydrated varieties, it will be found useful to subtract 14 for each molecule of water in order to find the molecular volume and condensation of the anhydrous salt, though such a process must be applied with caution. Conversely, the condensation of the group to which a salt belongs being given, the molecular volume and density of any hydrated variety may be found by adding 14 for each molecule of water to the volume of the anhydrous salt. Avoiding the calculation of molecular volume, the densities of an anhydrous salt and its hydrated variety are connected by the following formulæ, where w is the molecular weight of the anhydrous salt, d its density, n the number of molecules of water, and d_1 the density of the hydrate:—

$$d_1 = \frac{d(w+18n)}{w+14nd},$$

$$d = \frac{wd_1}{w+18n+14nd}.$$

Double Salts, Acid and Basic Salts.

Double salts have molecular volumes which are the sum of the molecular volumes of the constituent salts, any variation being amply explained by change of crystalline structure. Thus, $Al_2F_6 - 6NaF = 145 = 54 + (6 \times 15{\cdot}2)$, the molecular volumes of the two fluorides. The fact is of use in finding volumes which are not known in the solid state. $KBF_4 = 50{\cdot}5$, $KF = 237$; therefore $BF_3 = 26{\cdot}8$ as a solid, which gives it a density of 2·56, and the same condensation as aluminium fluoride. Similarly, from the fluorides and silicofluorides of rubidium, barium, and nickel we get $SiF_4 = 29$. Calcium gives $SiF_4 = 44$, but the density is obviously wrong, as the molecular volume of calcium silicofluoride appears greater than that of the barium salt. The specific gravity of the calcium salt is probably nearer 3·4 than 2·7.

Ferric and cobaltic cyanide can be found from the cyanides, ferricyanides, and cobalticyanides. $K_3Fe(CN)_6 = 182$; $3KCN = 43$, therefore $Fe(CN)_3 = 53$; $K_3Co(CN)_6 = 174$, therefore $Co(CN)_3 = 45$; $Ni(CN)_2.2KCN = 124$, therefore $Ni(CN)_2 = 38$.

The molecular volumes of basic salts are the sum of the normal salt and the oxide with which it combines.

Thus, basic copper iodate—

$$= CuOHIO_3 = \tfrac{1}{2}\{Cu(IO_3)_2 + CuO + H_2O\} = \tfrac{1}{2}\{78{\cdot}5 + 12{\cdot}5 + 14\} = 52{\cdot}5,$$

which is the volume of the basic salt. By this means one might obtain the densities of normal uranium salts from their uranyl derivatives but for the fact that the latter melt or decompose at temperatures below 100°.

Acid salts are difficult of treatment because few acids are solid at normal temperature, but acid ammonium tartrate and acid ammonium sulphate agree with the sum of their constituents as solids.

A curious fact concerning acid and basic salts is that they often have the same density as the normal salt with 1 molecule of water of combination. Thus, $KHCO_3$ and $K_2CO_3.H_2O$ have a density 2·17, KHC_2O_4 and $K_2C_2O_4.H_2O$ are both 2·08, $CuOHIO_3$ and $Cu(IO_3)_2.H_2O$ are 4·88. This coincidence, together with the fact that monohydrated salts vary most from the average of 14 for water, suggests that "water of constitution" is something more than a mere phrase.

(To be continued).

THE ERROR OF EXPERIMENT IN AGRICULTURAL FIELD TRIALS.*

By A. D. HALL, F.R.S., and E. J. RUSSELL, D.Sc.

ANALYSIS of the causes of error show that they fall unde several heads:—

(*a*) *Lack of Uniformity in the Soil.*—Even on a level field where no obvious variation occurs analysis shows that there are certain differences in different parts of the field. A sensitive and at the same time simple test is to ascertain the percentage of moisture in samples of soil collected to the same depth—6 or 9 inches—and as nearly as can be at the same time. The differences commonly amount to 5 (or in dry fields to 10) per cent of the moisture present. Another factor greatly influenced by variations in the soil is the amount of nitrate present. This affords an even more sensitive index of variation, since it depends on all the conditions favouring plant growth—moisture, temperature, air supply, and food-stuffs, these being necessary for the production of nitrate—and also on the amount of water washing through the soil, nitrates not being retained like ammonium salts. Here, also, differences are found of the order of 5 or 10 per cent of the amount present on fields that appear to be uniform. These differences may be accentuated where there is a dip in the field.

Variations in the field arise partly from natural and partly from artificial causes. So many agents come into play in soil formation that uniformity can hardly be expected. Further, the purely artificial operations, such as tilling, cropping, manuring, and folding, have a profound effect on the soil, persisting for some years. Frequently the treatment has not been uniform over the whole field. Drainage, whether artificial or natural, is rarely uniform; during a very wet winter it is not uncommon to see places in the field where wheat has been affected by differences arising either from lines of good drainage or patches of bad drainage. In other seasons the differences still exist, though not to so marked an extent.

(*b*) *Lack of Uniformity in the Conditions of Growth.*—The conditions of the outside row of a plot differ from those obtaining inside the plot, and those on the outside of the field are much modified by the competition of hedges and trees. These difficulties can, however, be obviated. The unequal incidence of disease is sometimes very troublesome.

(*c*) *Effect of Season.*—In manurial trials it is possible after a number of years to allow for the effect of season in a general way, especially as our knowledge of the properties of fertilisers increases. But in variety trials the problem is much more difficult, and cannot yet be said to be solved.

Total Magnitude of the Error of Experiment.—An examination of the Rothamsted records shows that the error is 10 per cent on plots where the past treatment has for many years been uniform, where all weighing, measuring, and other operations are performed with the utmost care, and where the general conditions are favourable for experimental work. Having regard to these considerations and the difficulties often encountered in field trials, the authors would not be prepared, as a general rule, to lay stress on differences of less than 15 per cent.

Some Complex Metallic Cations.—W. Herz.—By allowing silver nitrate solution to drop into ammonia solution until a permanent precipitate was obtained, the author obtained results which point to the formation of the complex cation, $Ag(NH_3)_2$. Similarly, with ethylamine, 1Ag2Amin, is formed, and with copper sulphate and ammonia the results correspond to the formula $Cu(NH_3)_4$. —*Zeit. Anorg. Chem.*, lxvii., No. 2.

* A Paper read before the British Association (Subsection B), Sheffield Meeting, 1910.

ADDITIONAL REFRACTIVE INDICES OF QUARTZ, VITREOUS SILICA, CALCITE, AND FLUORITE.*

By J. W. GIFFORD.

Reference is made to two previous papers (*Proc. Roy. Soc.*, February 13, 1902, and March 3, 1904) by the author, the latter in conjunction with the late Mr. W. A. Shenstone, F.R.S., who himself prepared the vitreous silica used.

In these papers the refractive indices of the above substances for 26 wave-lengths are given, and the first of them contains a full description of the special method of measurement adopted.

At the suggestion of Dr. T. Martin Lowry (*Proc. Phys. Soc.*, June 25, 1909), seven other wave-lengths of more recent importance have been added, and are now offered.

Table of Refractive Indices.

Wave-length.	Fluorite.	Quartz (ordinary ray).	Quartz (extraordinary ray)	Calcite (ordinary ray).	Calcite (extraordinary ray).	Vitreous silica.
6708 Li	1·4322578	1·5414590	1·5504717	1·6536691	1·4842714	1·4560717
6438 Cd	1·4327171	1·5423085	1·5513532	1·6550280	1·4846803	1·4567710
5461 Hg	1·4349895	1·5461684	1·5553393	1·6616473	1·4878900	1·4601545
5086 Cd	1·4361936	1·5482355	1·5574790	1·6652675	1·4895396	1·4619030
4800 Cd	1·4369095	1·5501317	1·5594492	1·6686130	1·4911018	1·4635705
4359 Hg	1·4395206	1·5537968	1·5632274	1·6751756	1·4941037	1·4667412
4046 Hg	1·4415296	1·5571506	1·5667107	1·6813434	1·4969064	1·4696753

Several of them, especially those in the spectrum of mercury, promise from their extreme brilliancy to be of more than usual value.

The method of measurement employed is identical with that described in the papers referred to; and the same prisms and instruments have been used, as well as a larger goniometer, with telescope and collimator of 30 inches focus, described elsewhere (*Proc. Roy. Soc.*, June 28, 1906), and used for checking the work. The measure of error is also of the same order, but the figures given point to the greater accuracy of the smaller instrument on which these and previous refractive indices have all been measured.

A table of the additional refractive indices is here given.

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,†

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, &c.

By PERCY H. WALKER.

(Continued from p. 174).

4. *Sedimentation Test.* — (a) *Apparatus.* — (1) Glass stoppered cylinders, graduated for 200 cc. and fractions thereof, the distance between the bottom and the 200 cc. mark being 25 cm. (10 inches). If unobtainable, other cylinders may be substituted, marks being placed at distances 25 cm. (10 inches) and 16 mm. ($\frac{10}{16}$ inch) from the bottom. (2) A pair of dividers with arms 15 cm. long or longer. (3) A millimetre rule. (4) Pipettes made from straight tubing (7 mm.), at least 30 cm. in length and having a capacity of from 10 to 15 cc.

(b) *Determination.*—By means of the special pipette introduce carefully, drop by drop, into one of the 200 cc. cylinders, exactly 16 mm. depth of the ink to be tested. The ink should be previously tested to determine a proper solvent for both base and dye. Alcohol is generally the solvent to use for rosin inks. It may be necessary to use other solvents, such as gasoline (boiling-point 50° to 60° C.), ether, benzol, &c. Dissolve the ink in the cylinder in the appropriate solvent and dilute up to the 200 cc. mark, stopper, and shake thoroughly. Allow the cylinder to stand, and record from time to time, by using the dividers and millimetre rule, the height of the top of the layer of sediment which collects in the bottom of the cylinder, expressing results in millimetres. During the first hour observations should be made at intervals of fifteen minutes; later, each hour for several hours successively, and then twice daily for a week to ten days.

After the settling of the top of the layer of sediment has entirely ceased, the height of the sediment should equal or exceed 16 mm., the amount of ink taken for the test. The rate of sedimentation is an index of the state of division of the carbon, some inks showing no appreciable layer at the expiration of a ten-day test.

In the case of some inks the supernatant liquid above the sediment is of such a dark colour that there is difficulty in locating the top of the sediment, even when the cylinder is inspected by light reflected at various angles. In this event the use of a dark room with a light placed so as to give a strong ray through a small aperture will locate the top of the layer of sediment in all cases except when the ink contains a very large percentage of a dense dye.

Frequently the layer may be located by holding an incandescent electric light back of the cylinder and noting where the carbon filament cannot be seen. The test is somewhat crude and only approximate, but it serves to give an idea of the fineness and amount of carbon, and, as a rule, agrees fairly well with the carbon determinations.

5. *Determination of Lampblack.*—Load a porcelain Gooch with asbestos, using a felt about one-fourth of an inch thick. After washing the felt thoroughly with water to remove fine particles, finally wash with alcohol and ether, dry, and weigh. Weigh out about 5 grms. of ink in a small beaker, dilute with a suitable solvent (alcohol is used in case of rosin-oil inks), transfer to the Gooch, and wash until all oil and soluble colour is removed. Finally, wash with alcohol and ether, dry, and weigh.

6. *Determination of Ash.*—The lampblacks prepared for the manufacture of cancelling ink yield less than 0·5 per cent of ash when burned, and the coal-tar dyes employed should contain no mineral matter other than that which is an essential part of the molecules of the substances to which the tinctorial power of these dyes is due. For the determination of the ash, place 2 to 3 grms. of the ink in a porcelain dish, which must be of such size as to avoid loss of ink due to the foaming which is likely to attend the beginning of the incineration. Heat the dishes thus charged in a muffle at a low red heat, until all organic matter and uncombined carbon have been burned. Cool and weigh. If an excessive percentage of ash is found, the percentage of mineral matter contained in the alcohol extract should be determined by incineration of the residue obtained after evaporation of this extract. If either the total ash or the ash of the alcoholic extract is high, a qualitative examination should be made.

7. *Resistance of Pigments and Dyes to Light and Reagents.*—It is necessary in the case of cancelling inks, and important, if not necessary, in the case of many stamping inks, that the pigments and dyes employed in their manufacture be as resistant as possible to means which may be employed for the erasure of marks made with them on paper. Under this heading may be mentioned also the importance of the use of dyes which

* A Paper read before the Royal Society June 23, 1910.

† *Bulletin* No. 109, Revised, U.S. Department of Agriculture, Bureau of Chemistry.

possess considerable affinity for vegetable fibres. It is not practicable to enumerate the agents which should be employed in experiments to ascertain the resistance of a given dye to erasure, as light, heat, and all of the solvents and reagents known to the chemist are available for the use of persons who might desire them for use in assisting them in making fraudulent erasures.

For the purpose of cancelling postage stamps, it is necessary that the cancelling marks be substantially indelible, because the inks used in printing many of the stamps are very resistant. Stamping inks used for other purposes, however, do not require absolute indelibility.

In making the tests use several layers of blotting-paper as a pad, pour on this a small quantity of the ink and distribute carefully; see that all excess has been absorbed by the pad before using the stamp. Make a sufficient number of impressions at one time to suffice for all tests and leave some in reserve. Having made the impressions, arrange them in groups according to the colour and kind of ink, and rank them according to the following scheme:—(1) Of highest rank; (2) very good, but not of the best; (3) good; (4) fair; (5) poor.

Having exposed the impressions to the various reagents, as described hereinafter, each sample is again rated according to the effect of the reagents, as follows:—(1) Unaffected; (2) slightly affected; (3) much affected; (4) almost effaced; (5) effaced.

The wet reagents used are pure water, water with the addition of 10 per cent of strong ammonia (sp. gr. 0·90), pure alcohol (95 per cent), alcohol with the addition of 10 per cent of strong ammonium hydroxide, 2 per cent hydrochloric acid, and 200th-normal bleaching powder. Expose each impression in a small Erlenmeyer flask to about 50 cc. of the reagent for twenty-four hours, noting its appearance at the end of fifteen minutes, one hour, and twenty-four hours. Then rinse, dry, and rate.

For the sunlight test expose impressions under glass for ten days to direct sun, rating at the end of the third, seventh, and tenth days. The tests with reagents are considered of less use than the other tests, and are not always applied.

Rubber-stamp Inks.

1. *Preparation and Care of Sample.*—The precautions given in regard to the care of samples of inks made with an oil base should be observed.

2. *Change of Weight on Exposure to Air.*—This determination should be conducted in the manner described for the determination of volatile matter in inks made with an oil base. Rubber-stamp inks, however, gain or lose in weight according to the constituents used in their manufacture and according to atmospheric conditions. A rubber-stamp ink should not, however, undergo very much greater changes in weight when exposed to the air under given conditions than diluted glycerin containing 75 per cent of glycerin and 25 per cent of water by volume.

3. *Penetrating Power.*—This test should be conducted in the manner described for inks made with an oil base.

4. *Sedimentation Test.*—This test should be conducted as described for inks made with an oil base, with the exception that the portions of ink should be diluted with water instead of with organic solvents.

5. *Determination of Lampblack and other Constituents.*—A scheme of analysis similar to that described for inks made with an oil base should be employed. Some experiments will be necessary in most cases to ascertain the proper solvent to be used in the case of each sample of ink to be examined. Alcohol, however, will generally be found to be satisfactory for rubber-stamp inks. This test is difficult and cannot be carried out without a slight loss. To make the loss as small as possible use a very thick felt of asbestos and make the filtration continuous—never allow the Gooch to run empty; if this occurs it is generally better to repeat the test.

6. *Resistance to Light and Reagents.*—The remarks made in regard to the investigation of the resistance of cancellations made with oil inks apply in general to cancelling and other inks for use with rubber-stamps.

To be continued).

"THE ENCYCLOPÆDIA BRITANNICA." ELEVENTH EDITION.

The University of Cambridge has taken over the control and copyright of the "Encyclopædia Britannica," and will publish a new and complete edition about the end of the present year. This Eleventh Edition, which has been eight years in preparation, entirely supersedes preceding editions, and is a wholly fresh and original survey of all existing knowledge in every field of human thought, research, and achievement. It will be comprised in 28 quarto volumes, of which the last will be devoted to a full and comprehensive index.

Preparations for this Eleventh Edition, on a very elaborate and costly scale, were begun by *The Times* in May, 1903. A large and competent staff, under the editorial management of Hugh Chisholm, one of the editors of the Tenth Edition, was set to work at Printing House Square, reinforced by eminent specialist advisers outside the office, as well as by some 1500 distinguished contributors in all parts of the world. As, however, the magnitude of the task and the authoritative nature of the growing work made themselves increasingly apparent, it was rightly felt that the enterprise was too vast to be a permanent addition to the manifold activities of a great newspaper. It was also realised that the proper origin and abiding-place for the foremost work of reference used by English-speaking people throughout the world was not a newspaper office, but a great learned institution. The University of Cambridge, whose authorities were fully satisfied with the solid and scholarly foundations laid by *The Times*, has decided to take over the copyright and control of the entire work, the connection between *The Times* and the "Encyclopædia Britannica" having ceased on January 1st, 1910. The Eleventh Edition of the "Encyclopædia Britannica" will therefore be issued as a complete work, in twenty-eight volumes, by the University of Cambridge about the end of this year.

In the course of the last hundred and forty years, during which ten editions of the "Encyclopædia Britannica" have been produced, that work has won a well-deserved reputation as the foremost and most comprehensive and trustworthy of encyclopædias in any language. It has come to be regarded not merely as a register of scientific progress but as an instrument of that progress, thanks to the fact that its contributors have mainly been the men who are themselves engaged in the task of advancing contemporary knowledge, whether of the past, as in history and its allied subjects, or of the present and the immediate future, as in what is specially called by the name of science and its applications. The experience which has been gained in the difficult art of encyclopædia-making by successive editors since 1768, no less than the high authority of the name of the "Encyclopædia Britannica," are both of the highest value for those engaged in the production of a new work of reference which is to hold an unquestioned superiority. When the opportunity of publishing the "Encyclopædia Britannica" was offered to the University of Cambridge, it was felt that the occasion had presented itself for a further and epoch-making advance in the great secular movement of University extension, in a wider sense than is usually attributed to that phrase.

In the past the "Encyclopædia Britannica" has been carried on as a private enterprise, and has hitherto been subject to many commercial vicissitudes. Six different publishers were concerned in the production of the ten previous editions; but it is now hoped that the work has found a per-

manent abiding-place at Cambridge. Its reception there sets the crown on the educational work done in the past by that important department known as the Cambridge University Press. The task accomplished in the past—by the publication of such works as the Cambridge Modern History, the Cambridge History of English Literature, and the collected works of leading men of science, such as Adams, Cayley, and Rayleigh—is now to be continued by the publication of a general digest and conspectus of all existing knowledge, such as can only be found in the pages of an adequate encyclopædia; this the Syndics of the University Press believe to be contained, in a lucid, comprehensive, and trustworthy form, in the 26,000 pages of the Eleventh Edition of the "Encyclopædia Britannica."

The publication of this Eleventh Edition of the "Encyclopædia Britannica" is a natural step in the evolution of the University as an educational institution and a centre of research. It will be offered to the public by the University of Cambridge, in the hope and belief that it will be found to be a trustworthy guide to sound learning and an instrument of culture of world-wide influence.

In many important departments of human knowledge—the perspective of history, the "values" of art and literature, the foundations of theology and Biblical criticism, the theory and applications of physical science—the attitude both of the expert and of the public has changed so remarkably since the Ninth Edition was in preparation that the "Encyclopædia Britannica" could only preserve its own position as the standard of authority by being re-made substantially as a new work. The very foundations of human knowledge have been laid afresh in the last thirty or forty years, and a change has passed over the whole field of learning, theoretical as well as practical, which could not be adequately expressed by mere revision. In the domain of science this is at once apparent; but it is equally true of history, in which the exact study of sources and the discoveries of archæologists have revolutionised the point of view. The enlarged disclosure of pre-Hellenic civilisation has made it necessary to write anew the whole of the articles dealing with early Greek history and culture; and so with innumerable subjects throughout. In this great task the editors have fortunately had resources at their disposal which were undreamt of by any of their predecessors. Their net has been cast over a wide area, of which the University of Cambridge forms only one centre. The whole world of learning has been at their disposal, and from a merely national the "Encyclopædia Britannica" has now become an international undertaking. Just as an English University often goes outside its own schools for professors and lecturers, so the editors of the "Encyclopædia Britannica" have drawn, not upon Cambridge alone, but upon many other Universities, such as Oxford, Edinburgh, Manchester, Paris, Berlin, Göttingen, Vienna, Milan, Harvard, Yale, Chicago, Columbia, and Kyoto.

The new work thus collects not merely the garnered knowledge of some 1500 distinguished contributors, but also the combined and cosmopolitan learning of those numerous institutions of research, under whose auspices to-day the bulk of original work is done—too often to remain a sealed book to the public. In more than one department the new "Encyclopædia Britannica" has been deliberately made the medium through which hitherto unpublished theories and discoveries are now first made accessible to the world. Thus it has been possible for the editors to aim at producing a new work under a famous old name, reproducing its best features under improved conditions, rather than a new edition in the sense commonly applied to books.

The most important of the new features which will signalise the publication of the Eleventh Edition of the "Encyclopædia Britannica" by Cambridge University is the fact that the whole of the work has been in progress and is published at the same time. Eight years have been devoted to the task of simultaneous construction of the entire work, in twenty-eight volumes, under the guidance of an exceptionally large and efficient editorial staff, and with the assistance of some 1500 contributors, representing the scholarship of every important University and other centre of research in the civilised world, and also representing the practical knowledge acquired in all the great engineering, manufacturing, and commercial enterprises of the twentieth century. Never before has it been possible, owing to the conditions of publication, to exercise a real editorial control over the whole of the "Encyclopædia Britannica"—or indeed any important encyclopædia—at one time and as a whole. The usual plan of publication by instalments spread over a series of years compelled the editors to deal with each successive volume as practically a separate unit, and a considerable amount of repetition was inseparable from this plan since a contributor writing for an early volume could not possibly tell—any more than the editors themselves could tell—what exactly would be the boundary line between his article and that of another contributor in a later volume on another branch of the same subject. Further, when the production of a great encyclopædia is spread over many years, there are bound to be many inconsistencies between early and later articles, due to the change which comes over not only the subject-matter but the theories of almost every branch of knowledge in the course of a decade. It is inevitable that discrepancies, seriously affecting the value of the complete work, should creep into an encyclopædia which takes nearly twenty years to make, and is published by instalments. The Ninth Edition of the "Encyclopædia Britannica" illustrates this tendency all the more, perhaps, because there was an actual change of editorial control in the course of the work. In the case of the Eleventh Edition, however, the decision to issue the work as a whole made it not only possible but necessary to plan it as a whole, and to deal with the contributors as the constituent parts in one great simultaneous enterprise. The whole of the MS. has lain under the editorial survey at one time—as if it were all spread out on one vast table—and the editors were thus able to avoid repetitions, to investigate and reconcile inconsistencies—often thus eliminating error—and to see that the scale of the whole work was preserved in each article, during the actual progress of the work, and before a single line had been sent to the printer. The current index, which was a novel and invaluable feature of the editorial work, was specially helpful to this end; the articles were indexed as they came in, while the work was in progress, and the duplications and inconsistencies which are apt to creep into a great work of reference were thus checked at the fountain-head. The editors believe that, as one consequence of this novel but scientific method of simultaneous construction, they have been able to present twice as much really independent information as the Ninth Edition contained although the Eleventh Edition will occupy but little more space than that work—twenty-eight volumes as against twenty-five. It is the constant tendency of the "Encyclopædia Britannica" to increase in size, for the simple reason that the knowledge of the world is continually growing in amount, and it has all to be dealt with in this work. But a serious effort has been made to keep the bulk of the work as small as is possible, consistently with adequate completeness, and the effectual prevention of repetitions has been extremely conducive to this end. It should also be added that the elaborate editorial planning of the whole work in advance, and the laying out at one time of the various articles in every department under the guidance of specialist advisers, enable all the contributors to work with a thorough comprehension of what their collaborators were simultaneously doing in other and allied branches of exposition. Only by such a method, dependent on the simultaneous preparation and publication of the complete work, is it possible to ensure that unity of treatment which is so often the chief desideratum in a great co-operative work of reference, and to make a living book in contradistinction to a mere heterogeneous collection of expert knowledge.

The advantage which has resulted to the work itself from the decision that it should be edited and written as a complete whole offers a corresponding advantage to the early purchaser of the Eleventh Edition of the "Encyclopædia Britannica," since it follows that the University of Cambridge is able to issue the work at once. The entire twenty eight volumes have practically left the hands of the editors, and are in course of manufacture, so that the work, which brings its survey down to the summer of 1910, will be issued as a complete whole about the end of the same year, or at latest in the first months of 1911. The advantages to the reader of simultaneous production of the entire twenty-eight volumes are too apparent to need description. It is only necessary to state that no new and important work of reference, at all comparable with the "Encyclopædia Britannica," has ever been originally issued as a complete whole. The Ninth Edition of the "Encyclopædia Britannica" was in course of publication for thirteen years; the "Dictionary of National Biography" for sixteen; the "Oxford English Dictionary," still unfinished, for twenty-two. There is no reason in the nature of things why a work of reference should be issued in periodical instalments, and it is clearly a serious inconvenience to all who use it that it should be long incomplete on their bookshelves.

One other striking innovation will signalise the association of the University of Cambridge with the "Encyclopædia Britannica." In the past the volumes of the "Encyclopædia Britannica" have been so large and weighty as to make it impossible to read them with any comfort, or even to consult them without resting them on a desk or table. Yet the "Encyclopædia Britannica" has always been a work which should be read for its interest and literary merit, as well as used for the purposes of reference. The publishers believe that it will be possible, without departing widely from the old size of the page and whilst maintaining the legibility of the type, to abolish this drawback. This they propose to do by the use of India paper, already well known from its adoption for expensive Bibles and other books in which it is desired to minimise weight and thickness. The India paper which has been chosen for a special impression of the new "Encyclopædia Britannica" combines toughness and opacity at least equal to those of the best ordinary printing paper with remarkable thinness and lightness, so that a volume on India paper will be less than one-third as thick as an ordinary volume containing precisely the same number of pages, and the average weight of such a volume will be less than one-third that of a volume on the ordinary paper. In order that the owner of the new "Encyclopædia Britannica" on India paper may derive the maximum of advantage from its use, it has been decided to bind this impression in full flexible leather—sheepskin or genuine morocco, according to price—in such a fashion that the India paper books may be bent back double, cover against cover, and held conveniently without any danger of injury in one hand. By the adoption of India paper, the "Encyclopædia Britannica" will therefore for the first time have a chance not only of being used as the leading work of reference, but also of being read as a storehouse of most entertaining and educative knowledge. This important aspect of the work has never found adequate recognition hitherto, simply on account of the physical difficulty of handling the old-fashioned heavy and cumbrous volumes. The publishers therefore feel justified in laying stress on a mechanical improvement which will probably he found largely to increase the value of the work. It may be added that this innovation will make it much easier to find shelf-room for the "Encyclopædia Britannica," as the complete set of twenty-eight volumes on India paper will only occupy two feet of linear space, as against nearly six feet for the impression on ordinary paper; and for the first time the "Encyclopædia Britannica" will be found a comparatively portable work, as its total weight will not exceed 60 lbs., while the ordinary paper impression will weigh more than 200 lbs.

NOTICES OF BOOKS.

The Elements. By Sir WILLIAM A. TILDEN, F.R.S., D.Sc. Lond., Hon. Sc.D. Dub., D.Sc. Vic., Ll.D. Birm. London and New York: Harper and Brothers. 1910.

THIS book contains an interesting and stimulating account of modern views as to the nature and origin of the elements, and the educated public will be able to get from it a clear conception of the main arguments which have been brought forward to establish the evolution of matter and the formation of the elements by a process analogous to condensation. A very slight acquaintance with chemistry will be sufficient to enable the reader to follow easily and profitably the accounts of the Atomic Theory of Dalton, the Periodic System and Theories of Evolution, culminating in an excellent summary of the Corpuscular Theory of Matter. The last chapter, in which the author puts forward some speculative views as to the evolution of the elements, will be read with the keenest interest, and the book will be greatly appreciated both for the lucid discussion it contains of the theory of inorganic evolution, and for the suggestions which the author has to offer towards the solution of the problem.

Notions Fondamentals de Chimie Organique. ("Fundamental Conceptions of Organic Chemistry"). By Ch. MOUREU. Third Edition. Paris: Gauthier-Villars. 1910.

THE author of this work aimed more particularly at producing a text-book of organic chemistry in which details were as far as possible avoided, and stress was laid upon general principles. The success of the earlier editions showed that he was correct in believing that there was room for such a work, and he has been well advised to preserve the same general plan in the third edition, to which many important additions have been made. Thus osmotic pressure and molecular refraction are treated more fully than before, and accounts are given of catalytic reactions and of the use of organo-magnesium halogen compounds. Recently discovered compounds and groups of compounds, such as the ozonides, carbon suboxide, the polypeptides, azomethane are described, and an excellent alphabetical index concludes the book, which may conveniently be used either as an aid to the study of original papers or as an introduction to more advanced works.

Die Brown'sche Bewegung und die Wahre Existenz der Moleküle." ("The Brownian Movement and the Real Existence of Molecules"). By Prof. Dr. J. PERRIN. Translated into German by Dr. J. DONAU. Dresden: Theodor Steinkopff. 1910.

THIS monograph is a reprint from the *Kolloidchemische Beihefte*, and the importance of the work it describes is ample justification for its publication in separate form. After giving a brief preliminary account of the phenomenon of Brownian movement the author proceeds to show that the study of suspensions provides an experimental basis for the molecular theory of matter. He explains methods of determining the magnitude of molecules, and pays special attention to the work of Einstein on the subject; the application of Stokes's law to microscopical magnitudes is also discussed, and it is shown that the gas laws may be applied to suspensions. The monograph is clearly written and excellently arranged, the text being divided up into short sections, and the author has done a valuable work in summarising his own results and those of other investigators and putting them before the scientific world in this convenient shape.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académié des Sciences. Vol. cli., No. 5, August 1, 1910.

Action of Mixtures of Carbon Monoxide or Dioxide and Hydrogen on Oxides of Iron.—A. Gautier and P. Clausmann.—When carbon monoxide and hydrogen act on Fe_3O_4 heated to 500°, a mixture of carbon (7 per cent), iron protoxide, and carbide of iron is obtained, the last two constituents being present in equal amounts. No free iron is obtained. The carbide of iron has the composition $Fe_{12}C$, and is decomposed by acids giving methane and hydrogen in the proportions of 1 to 10. Carbon dioxide and hydrogen at a red heat act similarly on iron, the dioxide being first reduced to the monoxide with the formation of oxide of iron. When carbon monoxide and hydrogen saturated with water-vapour act on iron sesquioxide, a substance is obtained on distillation which appears to resemble the paraffins, but it has not yet been identified.

Catalytic Preparation of mixed Oxides of Alcohols and Phenols.—Paul Sabatier and A. Mailhe.—When thoria acts on an alcohol, thorinate is obtained; this reacts with a phenol to give a mixed oxide, the thoria being regenerated:—

$$2C_nH_{2n+1}.OH + ThO_2 = ThO(OC_nH_{2n+1})_2 + H_2O,$$

$$ThO(OC_nH_{2n+1})_2 + 2R'OH = 2(R'O.C_nH_{2n+1}) + ThO(OH)_2,$$

$$ThO(OH)_2 = ThO_2 + H_2O.$$

The authors have thus prepared many mixed oxides; *e.g.*, anisol, $C_6H_5.O.CH_3$. With polyphenols no mixed oxides are obtained because the compounds formed with thoria are stable.

Disengagement of Heat in a Mixture of Radium and a Phosphorescent Salt.—William Duane.—When a known quantity of radium is mixed with a phosphorescent salt, the latter does not appreciably affect the disengagement of heat by the radium. There is no absorption of energy in the chemical reactions, and no chemical or atomic energy is liberated by the rays.

White, Red, and Pyromorphic Phosphorus.—Pierre Jolibois.—By studying the vapour tension curves and the critical points of phosphorus, the author has shown that pyromorphic phosphorus is stable below 450°, ordinary red phosphorus between 450° and 610°, and white phosphorus above 610°.

Heat of Combustion of Hydronaphthalene Derivatives.—Henri Leroux.—In the fatty series the addition of hydrogen to an ethylene compound is always exothermic (about 30 cal.). In the case of benzene the thermic values of the first stage of hydrogenation is 0·8 cal., differing from that of the second, 25 and 26·8 cal. In the hydronaphthalene series there are two minima, one corresponding to the production of naphthane tetrene and the other corresponding to that of naphthane diene. These facts show that Bamberger's formula for naphthalene is more probably correct than Erlenmeyer's.

Compounds of Thorium Chloride with Ammonia.—Ed. Chauvenet.—Three series of compounds of anhydrous thorium chloride and ammonia are formed. The first are obtained by treating thorium chloride with liquid ammonia, and then subjecting the product to progressively increasing temperatures, the second by allowing gaseous ammonia to act on thorium chloride, while some of the compounds of the second series unite with liquid ammonia to give rise to a third series of compounds which are isomeric with the preceding. The first series is composed of addition products, $ThCl_4 + nNH_3$, which are similar to the ammoniacal aluminium chlorides. The second group consists of more stable compounds which are not decomposed by water nor by the action of a vacuum. They may be represented by the structural formula $Th \equiv [NH_2(NH_4)Cl]_3$ $\backslash NH_3Cl$. The third series consists of addition products, $Th \equiv (NH_3Cl)_4 + nNH_3$. Above 120° only one ammoniacal derivative, $ThCl_4.4NH_3$, exists.

Catalytic Reactions in the Wet Way using Aluminium Sulphate.—J. B. Senderens.—In the preparation of ethylene from ethyl alcohol and sulphuric acid, aluminium sulphate acts catalytically, giving a much increased yield. Probably a double sulphate of aluminium and ethyl is formed and subsequently decomposed. $(SO_4)_3Al_2.SO_4HC_2H_5 = (SO_4)_3Al_2 + H_2SO_4 + C_2H_4$. If excess of alcohol is used the following reaction occurs:—

$$(SO_4)_3Al_2.SO_4HC_2H_5 + C_2H_5OH = (SO_4)_3Al_2 + SO_4H_2 + C_2H_5.O.C_2H_5.$$

Condensed products are formed as well as the hydrocarbons.

Mechanism of Photochemical Reactions and Formation of Vegetable Principles.—Daniel Berthelot and Henry Gaudechon. When the rays from a quartz mercury lamp act upon sugar solutions the following results are observed:—Glucose (aldehydic sugar) gives about equal volumes of carbon monoxide and methane, and six times as much hydrogen. Lævulose (ketonic sugar) gives about ten times as much CO as CH_4, the generation of gas being very rapid and vigorous. Maltose, which splits up into 2 molecules of glucose, gives the same gaseous products. Saccharose, which splits up into glucose and lævulose, gives the corresponding quantities of the gases.

No. 6, August 8, 1910.

Causes of Odour of Geranium.—G. Austerweil and G. Cochin.—The odour of geranium is always associated with the presence of the group = CH—CRROH. Nerol, which is an isomer of geraniol, smells of roses, and thus it probably contains the group $—CH_2—CH_2OH$.

Preparation of True Arbutin.—H. Hérissey.—From commercial arbutin true arbutin can readily be prepared by a method based upon the precipitation of its alcoholic solution by means of caustic potash. The yield is about two-thirds of the weight of the commercial product used.

Zeitschrift für Anorganische Chemie. Vol. lxvii., No. 2, 1910.

Reversible Action of Oxygen on Magnesium Chloride.—Wilhelm Hirschkind.—Moldenhauer has investigated the action of oxygen on magnesium chloride and of chlorine on magnesium oxide, and has determined the constant k_p from the equation $k_p = \frac{Cl_2}{O_2\sqrt{p_{O_2}}}$. The author has repeated the experiments, using both the dynamic and static methods, and modifying the experimental conditions and arrangement, and by the dynamic method has obtained results which agree very well with Moldenhauer's, but the amount of chlorine generated never reaches the equilibrium amount when oxygen or a mixture of chlorine and oxygen acts on magnesium chloride. This anomaly may be due to the formation of oxychloride. When chlorine acts on magnesium oxide or on a mixture of magnesium oxide and chloride, the values obtained for the constant seem to show that adsorption of the chlorine by the finely powdered oxide takes place. When the same solid substance is used for some time, whether it consists of magnesium chloride or of a mixture of equal parts of chloride and oxide, the constant, after originally having the normal values, sinks much lower, these lower constants being reached from both sides. Possibly this is to be explained by supposing that oxychloride is slowly formed from solid magnesium chloride and oxide.

Calorimetric Observations when Iron Oxide and Silver Hydrosol are Simultaneously Precipitated.—Fr. Doerinckel.—The simultaneous precipitation of iron oxide and silver oxide hydrosols is accompanied by a development of heat which the author has determined quantitatively. The results show that, as the percentage of silver is increased, the heat of coagulation increases to a maximum (between 60 and 70 per cent of silver.

Salts of a Hexa-acetato-tripyridine-trichrom Base.—R. F. Weinland and Ernst Gussmann.—When pyridine is added to a warmed concentrated aqueous solution of the biacetate of the hexa-acetato-trichrom base, $\left[Cr_3\begin{matrix}(CH_3COO)_6\\OH_2\\OH\end{matrix}\right](CH_3COO)_2+H_2O$, the liquid, which is originally dark green, changes colour, appearing dirty red in a deep layer, and light green in a thin layer. On cooling, green crystals separate out. These are the biacetate of hexa-acetato-tripyridine-trichrome base, $\left[Cr_3\begin{matrix}(CH_3COO)_6\\3Py\\OH_2\\OH\end{matrix}\right](CH_3COO)_2$. From the mother-liquor, which is dark violet, a basic acetate free from pyridine, $Cr_2\begin{matrix}(CH_3COO)_3\\(OH)_3\end{matrix}.9H_2O$, can be isolated. The authors have prepared and described many primary and secondary salts of the base, as well as one tertiary salt. The salts ormed with colourless acids are pale green, and yield aqueous solutions which are dirty red in transmitted light. Many of them are difficultly soluble. The aqueous solutions of the secondary and tertiary salts have an acid reaction, while the primary are neutral. When the aqueous solution of one of the salts is boiled, pyridine and acetic acid are driven off. With ammonia no chromic hydroxide is precipitated. Nitric acid and hydrochloric acid when heated decompose the base completely, giving chromic nitrate or chloride. The free base can be obtained by treating the iodide with silver oxide in aqueous solution. The tripyridine base is a stronger base than the hexa-acetato-trichrom base.

Behaviour of Lithium towards Sodium, Potassium, Tin, Cadmium, and Magnesium.—G. Masing and G. Tammann.—The accompanying table gives a summary of the compounds of magnesium, lithium, sodium, and potassium with the alkali metals, and with zinc, cadmium, tin, and lead. Lithium resembles magnesium more than sodium or potassium as regards its power of forming compounds. Lithium and magnesium form a series of mixed crystals, which is not a usual occurrence with metals of relatively low melting-point.

	Li.	Na.	K.	Zn.	Cd.	Sn.	Pb.
Mg.	O	O	O	$MgZn_2$	MgCd	Mg_2Sn.	Mg_2Pb
Li		O	O	—	LiCd, $LiCd_2$	Li_4Sn, Li_3Sn_2, Li_2Sn_5	—
Na.			X	$NaZn_{12}$	$NaCd_5$ $NaCd_2$	Na_4Sn, Na_2Sn, Na_4Sn_3 NaSn, $NaSn_2$	Na_4Pb, Na_2Pb, NaPb, Na_2Pb_5
K..				KZn_{12}?	KCd_{11}, KCd_7	K_2Sn?, KSn?, KSn_2, KSn_4	K_2Pb, X, KPb_2, KPb_4

Eosin Reaction of Glass at Broken Surfaces.—F. Mylius.—In an earlier communication the author has shown that, by using freshly broken surfaces of glasses in contact with moist ethereal solution, values can be obtained calorimetrically which correspond to the degree of weathering. These results, however, applied only to light glass. The investigation has now been extended to heavy silicate glasses. It has been found that in the weathering of heavy glasses a decrease of the natural alkalinity can be detected; it comes to a standstill after a week. To test the resistance to weathering of all technical glasses, the weathering in seven days at fresh fractures in water saturated with air at 18° is suitable. The corresponding eosin values are comparable, and give the weathering-alkalinity of the glass. Natural and weathering alkalinity are constant values by the comparison of which the chemical character of any kind of glass can be determined. Light boron silicate glasses often give high weathering alkalinity and low natural alkalinity, while the heavy glasses give the opposite result.

Explanation of the Unlimited Reducing Action of Organic Substances on Potassium Permanganate.—Anukul Chandra Sarkar and Jatindra Mohan Dutta.—When potassium permanganate acts on oxalic acid at 100° manganese dioxide is precipitated, and an unlimited amount of permanganate can be reduced. This reduction cannot be due to the corresponding oxidation of the organic substances. By direct experiment the authors have found that freshly prepared and washed manganese dioxide can reduce an acid solution of permanganate. All the reactions which occur when permanganate is added to a boiling solution of oxalic acid and sulphuric acid are expressed by the following equations:—

(*a*) $3[5C_2H_2O_4+2KMnO_4+3H_2SO_4 = 10CO_2+K_2SO_4+2MnSO_4+8H_2O]$

(*b*) $2[3MnSO_4+2KMnO_4+2H_2O = 5MnO_2+K_2SO_4+2H_2SO_4]$.

(*c*) $2MnO_2+2H_2SO_4=2MnSO_4+2H_2O+O_2$.

(*d*) $3MnSO_4+2KMnO_4+2H_2O = 5MnO_2+K_2SO_4+2H_2SO_4$.

The reductions (*b*) and (*c*) are repeated indefinitely.

Filtrate from Sulphuretted Hydrogen Precipitate.—Julius Petersen.—The author has worked out a new method of qualitatively examining the filtrate from the sulphuretted hydrogen precipitate. The filtrate from the sulphuric acid precipitate (barium and strontium sulphate) is evaporated to 30 cc., solid sodium carbonate is added, and 5 to 10 cc. of sodium hydroxide solution, and the whole is warmed. Sodium sulphide is then added in excess, and the precipitate formed is filtered off. The filtrate contains aluminium, which may be precipitated as hydroxide. The residue, consisting of CoS, NiS, FeS, MnS, ZnS, $Cr(OH)_3$, $CaCO_3$, $MgCO_3$, is treated with hydrochloric acid containing sulphuretted hydrogen. The insoluble residue consists of CoS or NiS. Sodium carbonate and hydroxide are added to the solution, when hydroxides and carbonates of Fe, Mn, Cr, Ca, Mg are precipitated, while Zn goes into solution. The residue is treated with sodium peroxide and filtered. If the filtrate is yellow, Cr is present (Na_2CrO_4). The residue, consisting of $Fe(OH)_3$, MnO_2, $CaCO_3$, $MgCO_3$, is dissolved in 5 per cent acetic acid containing 5 per cent of sodium phosphate. Ca and Mg go into solution as acetates, while MnO_2 and $Fe(OH)_3$ remain undissolved. If Co, Ni, and Cr are not present, the procedure can be much simplified.

THE CHEMICAL NEWS.

Vol. CII., No. 2655.

NOTE ON THE DETECTION OF NITROGEN IN ORGANIC SUBSTANCES.

By H. RUSSELL ELLIS, B.Sc., F.C.S.

A test given by V. Castellana (*Gazetta*, 1904, xxxiv. 357, and *Journ. Chem. Soc. Abs.*, II., 201, 1905) has been strongly recommended as an excellent means of testing for nitrogen in organic substances, and also for testing the same for halogens and sulphur.

The method employed is to heat a mixture of pure dry Na_2CO_3 or K_2CO_3 and Mg in a test-tube, on porcelain, or on platinum foil, and when the interaction between these bodies commences to add the organic substance. The Mg sets free K or Na, which, being nascent, combines readily with the carbon and nitrogen forming cyanide, and with the sulphur and halogens to form sulphide and halogen salts.

The method gave cyanide most readily with substances such as urea, nitrophenols, nitro-compounds including picric acid; these substances do not yield cyanide readily in the ordinary sodium test.

On testing pure samples of $CHCl_3$ and CCl_4 (Kahlbaum) for nitrogen by this method a copious precipitate of Prussian blue was obtained.

Other pure substances which were known to contain no nitrogen gave similar results.

The materials used (Kahlbaum) were quite free from cyanide, and before ignition gave no cyanide whatever; no reagent used contained any cyanide.

It was finally found to be formed during the action of the Mg powder on the carbonate from atmospheric nitrogen. If this reaction is allowed to take place slowly without largely exposing to the air, cyanide is formed; if violently with plenty of air, no cyanide at all. The same reaction takes place when mixtures of Mg and $CaCO_3$, Mg and $BaCO_3$, and Mg and $SrCO_3$ interact in contact with a small amount of air. In these cases cyanide, cyanamide, nitride, and carbide are formed.

It can be seen from the above that as a test for nitrogen the reaction given by Castellano is useless.

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THE MOLECULAR VOLUMES OF SOLIDS.

By H. H. STEPHENSON.

(Concluded from p. 180).

Condensation of Salts.

After this digression on the additive volumes of hydrated double acid and basic salts, we must return to the consideration of anhydrous salts. It was shown that oxides undergo condensation according to their family. Salts which are formed by the combination of two elements, such as chlorides and sulphides, may be dealt with precisely like the oxides; that is, by taking the atomic volumes as given on Lothar Meyer's curve. The point of this paper is that order may be traced in the molecular volumes of solids without diverging from the atomic volumes of the free elements at normal temperature and pressure. In a very few instances it happens that the molecular volume is slightly greater than the sum of the atomic volumes. This may mean that expansion takes place on solidification, or that one of the atomic volumes is too low, but unless all the compounds of an element show abnormally low condensation, as in the case of the iodides, it is more probable that the density given is not quite accurate. It sometimes happens that densities given in text-books for anhydrous salts refer really to hydrated varieties, as in the case of antimony pentoxide mentioned previously.

In the following tables, the first column of figures refers always to the molecular volumes, the second to the condensations.

Chlorides, Cl = 24·6.

LiCl	21·2	44
Na	27	45
K	38·4	46
Rb	44·8	45
Cs	43	55
CuCl	27·3	14
Ag	26	25
Hg′	34	14
Tl′	34	19

The density of cæsium chloride is obviously wrong, and probably refers to the hydrate. Its real density should be 3·17, not 3·97 as given in Landolt and van Nostrand.

$MgCl_2$	44	31
Ca	49·3	36
Sr	52	38
Ba	54·3	37
$ZnCl_2$	47	20
Cd	49·6	20
Hg	51	20
Cu	44·3	21

The chlorides of the third and fourth groups are mostly liquids or solids of low melting-point, but $LaCl_3$ has M.V. 62·5 and C 35·3, and $ThCl_4$ M.V. 81, and C 32. $PbCl_2$ resembles $MgCl_2$—M.V., 47·8; C, 29; a condensation which is shared by the chlorides of iron and cobalt. The fifth group also—where the densities are known—are liquids except $BiCl_3$, M.V., 57·5; C, 40. In Group VI., we have $CrCl_2$ *v* 44·5, *c* 21·5, which is like the zinc group, and $MoCl_5$ 28·9 *c* 78—figures that make one sceptical of the density, 9·5, attributed to molybdenum pentachloride. The chlorides of the transition elements are:—

$MnCl_2$	50·8	10
$NiCl_2$	50·8	9
$FeCl_2$	42—50	11—25
$CoCl_2$	38·6	32
$PtCl_2$	45·5	22
$FeCl_3$	58	29
$CoCl_3$	56·5	30
$SmCl_3$	46·8	50

Such are the chlorides, and where a number of members of one group are known they bear out very well the hypothesis of equal condensation. They may be taken as a type of the salt formed by the union of two elements, of which other examples are bromides, iodides, fluorides, sulphides, borides, hydrides, carbides, selenides, tellurides, and arsenides. Some of the compounds of these radicles are so little known with regard to their densities that they do not repay enumeration. Others, such as the sulphides, bromides, and fluorides, obey the law of condensation, and do not require comment—save, of course, that each radicle has its own condensation factor. Thus the oxides of the sodium group undergo 60 per cent condensation, the chlorides 45, the sulphides 50, and so on.

But the iodides require a word to themselves, because many of them have molecular volumes greater than the sum of the atomic volumes if iodine be taken as 26. As remarked before, the point of this paper is that we take the atomic volumes of the free elements, but we are not required to take the value of any particular crystalline variety. The density which gives iodine the volume of 26 is that of the rhombic crystals, and we know that crystalline form may alter the density by 20 per cent. So that we are entitled to assume that amorphous iodine would have an atomic volume of 31, especially as Lothar Meyer's curve

allows considerably more latitude with regard to the volume of that element. The iodides then fall into line with other salts composed of two elements.

Complex salts in which the acid radicle consists of a number of elements as in sulphates, nitrates, or phosphates, present an apparent difficulty with regard to their theoretical volume. But a moment's reflection suffices to show that the theoretical volume of the radicle is the sum of the atomic volumes of its component elements, for if the molecular volume of the acid anhydride be taken it would be merely consistent to take also the molecular volume of the basic oxide, and we should revert to the old state of affairs. The radicles, SO_4, CO_3, PO_4, NO_3, must therefore be regarded as having the theoretical volumes 73, 50, 72, 60, respectively—figures obtained by adding up the atomic volumes of the component elements. Of these complex salts, the sulphates may be taken as a type.

Sulphates, $SO_4 = 73$

Li_2SO_4	50	50
Na	53	56
K	66	60
Rb	74	60
C	86	60
Ag_2SO_4	58	38
Hg′	66	36
Tl′	73·5	32
$BeSO_4$	?	—
Mg	44·7	49
Ca	47·3	53
Sr	51·5	52
Ba	54	51
$ZnSO_4$	43·5	47
Cd	44·6	48
Hg	46	48·5
Pb	47·3	48
$Al_2(SO_4)_3$	127	47
In	151	40
Er	173	40
Sc	147	40
Y	178	33
La	158	40
Ce	146	43
Pr	153	42
Yb	—	—
Gd	146	40
$Th(SO_4)_2$	100·4	40
$Sb_2(SO_4)_3$	107	58
$Cr_2(SO_4)_3$	131	45
$Fe_2(SO_4)_3$	129	45
$MnSO_4$	51	37
Fe	48·5	39·5
Co	44·8	44
Ni	45·5	43
Cu″	45·3	44

To give all the details of other radicles would expand this paper to the size of a book, but the reader has now had the opportunity of examining the molecular condensation of the oxides, chlorides, and sulphates, and is in a position to judge of the following hypothesis which, if confirmed, would become a law:—

Metallic oxides and salts undergo a molecular condensation on solidifying, which is the same in each group or subgroup of the Periodic Table, but varies with the groups and the particular class of compound concerned.

The natural consequence is that the density of any solid may be calculated from the condensation of its group if the atomic volumes of the component elements be known. Let us suppose, for the sake of an example, that the atomic volume of radium is 60, and that its salts fall in with the calcium-barium group. The molecular volume of the oxide will then be 35, of the nitrate 60, of the chloride 68, of the sulphate 64. Therefore their densities will be 6·9, 5·85, 4·4, and 5·1 respectively.

PERCENTAGE MOLECULAR CONDENSATION OF ANHYDROUS SOLIDS.

	Acetate, $C_2H_3O_2' = 45$.	Boride, B = 4·5.	Bromate, $BrO_3' = 68$.	Bromide, Br′ = 25.	Carbonate, $CO_3'' = 50$.	Chlorate, $ClO_3' = 67$.	Chromate, $CrO_4'' = 65$	Cyanide, CN′ = 24.	Fluoride, F′ = 16·7.	Formate, $HCO_2' = 36$.	Hydride, H′ = 1·4.	Iodate, $IO_3' = 71$.	Iodide, I′ = 31.	Nitrate, $NO_3' = 60$.	Nitrite, $NO_2' = 46$.	Oxalate, $C_2O_4'' = 69$.	Phosphate, $PO_4''' = 72$.	Pyrophosphate, $P_2O_7'''' = 131$.	Selenate, $SeO_4'' = 75$.	Selenide, Se″ = 18·5.	Sulphite, $SO_3'' = 59$.	Sulphide, S″ = 17.
Li, Na, K, Rb, Cs	(19)	—	53	35	56	54	55	(39)	63	(42)	0	53	26	56	53	52	58	58	57	—	(40)	53
Cu′, Ag, (Au), (H), Hg′, Tl′	7	—	32	14	34	36	—	0	19	—	—	36	0	42	39	33	33	33	27	5	19	0
(Be), Mg, Ca, Sr, Ba, (Ra)	(12)	23	—	27	53	50	46	—	53	36	20	48	17	55	—	(40)	54	46	48	—	34	37
Zn, Cd, Hg″, (Mg)	3	—	42	7	45	(51)	—	0	48	—	—	—	4	—	—	—	44	—	(29)	0	—	7
Mn, Fe″, Ni, Co, Cu, (Pb′), (Sn″)	0	18	41	19	43	(45)	(35)	—	42	28	—	45	—	(46)	—	(39)	48	47	—	33	—	14
Sc, Y, La, Ce‴, Yb‴, Gd, Sm, (Fe‴), (Co‴)	0	20	—	—	—	—	—	—	—	—	—	—	—	—	—	(33)	(33)	—	(42)	—	—	18

The sodium group also undergoes a condensation of 56 in the perchlorate ($ClO_4' = 82$), 51 in the periodate ($IO_4' = 84$), 48 in the permanganate ($MnO_4' = 65$), and 42 in the thiocyanate (CNS = 40). Oxides, chlorides, and sulphates have already been detailed in the course of the paper.

It follows also from our hypothesis that the atomic volume of any element can be found when the density of any of its compounds has been determined. Ytterbium, for example, has an unknown atomic volume. Its oxide, Yb_2O_3, has the molecular volume 43, and the condensation of the sesquioxides of its group is 48, which gives Yb = 19·8, showing a density of 8·7.

We are now in a position to understand the apparent equality of molecular volume of chemically similar and isomorphous salts in some cases, and their inequality in others. Turning back to the isomorphous series mentioned at the beginning of this paper, we find one series, $R_2SO_4.7H_2O$, whose molecular volumes are equal if the densities most favourable to equality be taken. But the density of the nickel salt is given as 1·93—2·04, which means that the molecular volume may be as low as 137. Similarly, the volume of the magnesium salt varies from 140 to 149, so that the volumes are not really equal, but may vary by at least 5 per cent. Now, if the sum of the atomic volumes of this series be taken, it will be found that they differ by less than 5 per cent, so that our condensation theory explains the apparent equality of volume because the salts have all undergone equal condensation from nearly equal theoretical volumes.

The other series, $R_2(SO_4)_3$, where the volumes were unequal, have already been dealt with in considering the condensation of the sulphates. The series obeys the law of equal condensation, but the molecular volumes are not equal, because the atomic volumes of the metals concerned differ appreciably.

It will be seen, then, that equality of molecular volume has less basis in fact than equality of condensation, and is also a serious departure in theory from the Periodic Law. Molecular condensation, on the other hand, offers a consistent explanation of molecular volume and density without diverging from the ascertained periodic character of atomic volume.

In the foregoing remarks we have thought it unnecessary to detail the molecular volumes and condensations of all radicles, but the appended table summarises the results of all the important classes of compounds in a convenient form, and the molecular volume and density of any solid can be found from it, remembering that double salts, acid, and basic salts, are approximately additive in volume, and that $H_2O = 14$. It will be seen that monovalent thallium and mercury agree very closely in condensation with the silver sub-group. Tutton has shown that the sulphates and selenates of rubidium, ammonium, and thallium have the same molecular volumes, and this is true also of the perchlorates and nitrates. Then, also, ammonium and thallium have the same volume in the bromides and chlorides, ammonium and rubidium in the iodide, permanganate, and acid tartrate. So that ammonium and thallium molecular volumes can generally be taken as equal to the rubidium salt. As thallium condensations average two-thirds of the corresponding silver salt, this means that the sodium and silver sub-groups of Group I. are connected in their condensation. If v be the theoretical volume of any radicle of valency n, c and c_2 the condensations of the sodium and silver groups respectively, then $\frac{100 - c_1}{100} \times (56n + v)$ and $\frac{100 - \frac{2}{3}c_2}{100} \times (17n + v)$ are the volumes of the rubidium and thallium salts. These are equal; therefore $\frac{2}{3}c_2 = \frac{c_1(56n + v) - 3900n}{17n + v}$.

The table gives the acid radicles in alphabetical order, the figures immediately beneath them being their theoretical volumes. Brackets denote that the data are insufficient to be reliable. The table refers only to anhydrous salts.

Summary.

Regularity may be traced in the molecular volumes of solids without departing from the atomic volumes of the free elements. The concept of molecular condensation is defined and shown to be equal for anhydrous salts in each group or sub-group of the Periodic Table for each class of compound, but to vary with the groups and with the acid radicle. The density and molecular volume of any solid compound may therefore be calculated if the group condensation be known. Unknown atomic volumes of elements may also be obtained from the density of any compound. The value for ytterbium is given.

Hydrated salts, double salts, acid and basic salts, are generally additive in molecular volume, the value for each molecule of water averaging 14. Formulæ are given connecting the densities of hydrated and anhydrous salts.

It is shown that the apparent equality of volume of some series of similar and isomorphous salts is due to the fact that they have undergone equal condensation from approximately equal theoretical volumes.

ON APPARATUS FOR THE PRODUCTION OF CIRCULARLY POLARISED LIGHT.

By A. ERNEST OXLEY, M.Sc., Trinity College, Cambridge.

IF we use a Fresnel's rhomb to produce circularly polarised light the transmitted beam is displaced laterally from the incident beam, and it is therefore necessary to readjust the successive pieces of apparatus if we are to keep the beam of light in the field of view as the rhomb is rotated. No such lateral displacement is experienced with a quarter wave-plate, but in this case we are limited to the use of monochromatic light. The idea of the present investigation is to devise a piece of apparatus which will produce a beam of circularly polarised white light without involving the inconvenience of the lateral displacement previously referred to.

Two pieces of apparatus have been devised with this end in view. In the first, two rhombs of glass are placed in contact as shown in Fig. 1. The beam of plane polarised white light incident at an azimuth of 45° with respect to the plane of the figure is reflected totally from the surfaces A, B, C, and D.

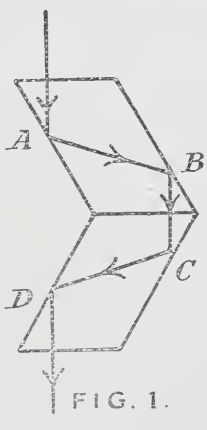


FIG. 1.

The glass used in constructing the rhombs had refractive index $\mu_{D1} = 1{\cdot}5035$, and the total phase difference introduced between the components polarised parallel and perpendicular to the plane of incidence amounts to $\pi/2$ when the angle of the rhomb has either the value 74° 38′·2 or 42° 34′·8. The larger of these values is chosen, for then the dependence of the phase difference on the wave-length is very small. In fact, with the large angle this form of polariser is twice as efficient as Fresnel's rhomb, but it has the disadvantage of being inconveniently large for a given aperture.

To overcome this diffiulty a second form of polariser has been devised in which three total reflections are used. The bi-trapezoidal form of the section is shown in Fig. 2.

If, as before, $\mu_{D1} = 1{\cdot}5035$, and the acute angle of the trapezoid be $73^\circ\ 48'{\cdot}6$, then the total phase difference introduced between the components polarised parallel and perpendicular to the plane of incidence, for the three reflections indicated, is $\pi/2$. The ellipticity of the transmitted light is smaller for a given wave-length than it is when a Fresnel's rhomb is used, and so this form is more efficient than Fresnel's rhomb. Moreover, this form possesses the advantage of compactness.

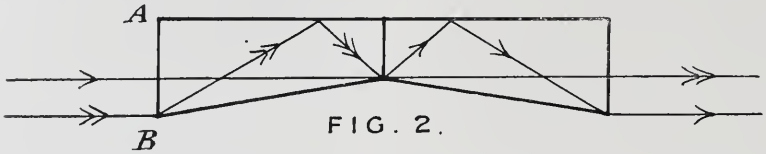


FIG. 2.

In the B.A. Report for 1851, Prof. G. Stokes claims a high degree of accuracy to be attainable by his elliptic analyser, but since it is somewhat difficult to make accurate settings of a quarter wave-plate and the analysing Nicol's prism, it was thought this second form of polariser would prove useful in the analysis of elliptic vibrations. One axis of the quarter wave-plate would be replaced by an edge of the glass, which should be specially worked, and accurate settings of this edge with respect to the analysing Nicol's prism could be easily made.

Owing to the fact that light polarised parallel to the plane of incidence is more copiously reflected on crossing the joint than the perpendicular component is, the transmitted light (for azimuth of 45°) would be slightly elliptically polarised, and it is necessary to correct for this by adjusting the azimuth of the incident vibration. The new azimuth may be found experimentally or by calculation. If ϕ be the angle of incidence of the beam on the joint, μ the refractive index of the glass with respect to air, and Ω the new azimuth with respect to the edge AB (Fig. 2), then—

$$\tan \Omega = \frac{1}{\cos^2 \{\phi - \text{arc . sin } (\mu \sin \phi)\}},$$

and taking $\mu = 1{\cdot}5035$, we find—

$$\Omega = 49^\circ\ 2'.$$

With this azimuth the transmitted components are equal in amplitude and differ in phase by $\pi/2$, and consequently the transmitted light is circularly polarised.

Each form of polariser is mounted in a metal cylinder provided with central apertures.

ON A NEW FORM OF WHITE LIGHT HALF-SHADE.

By A. ERNEST OXLEY, M.Sc., Trinity College, Cambridge.

THE arrangement of rhombs described in the first form of polariser may clearly be used to form a white light half-plate. Taking the refractive index of the glass as 1·5173, and the angle of the rhombs 55° 15·5′, the four total reflections produce a phase difference between the components amounting to π. The two blocks of glass C and D (Fig. 1) partly compensate for loss of light by absorption, but their chief use is to compensate for loss of light at the four reflections at normal incidence.

Half the field of view is occupied by the aperture of a rhomb, and the other half by either of the blocks C or D. By making the edge of the rhomb overlap the block slightly, the line of separation of the two halves of the field is made quite sharp.

This form of half-shade—using white light—has been compared with the Laurent half-shade—using monochromatic light—and was found to be quite as efficient as the Laurent. Since the cost of large blocks of calcite is becoming more prohibitive to their use, this form of white light analyser may prove useful for the ordinary laboratory determination of the rotation of the plane of polarisation.

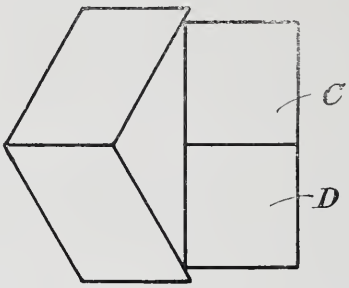


FIG. 1.

The length of the half-shade for an aperture of 1·6 cm. square is about 3 cm.

A RAPID PROCESS FOR THE ESTIMATION OF COCOANUT-OIL IN ADMIXTURE WITH BUTTER-FAT.

By NOEL C. CASSAL, A.R.C.S., B.Sc. (Lond.),
and
B. HENRY GERRANS, F.I.C.

THE determination of cocoanut oil when in admixture with butter-fat presents special difficulties, and a large number of processes for the estimation of the cocoanut-oil have been put forward, both in this country and abroad. Of the various methods, the most satisfactory are those which are based upon a consideration of the proportion of insoluble volatile fatty acids yielded on distillation under determined conditions. The titre of the insoluble volatile fatty acids obtained from cocoanut-oil is higher than that of the insoluble volatile fatty acids from butter-fat, but the extent of the difference shown in this respect is dependeut entirely upon the conditions of experiment.

Thus in Wauter's well-known method of double distillation (one of the best methods at present known, both from a manipulative and quantitative point of view), working on 5 grms. of filtered fat, a titration figure of 15·4 (cc. N/10 KHO) is obtained for the insoluble volatile fatty acids from cocoanut-oil, and a titration figure of 0·9 (cc. N/10 KHO) for the insoluble volatile fatty acids from butter-fat—a total difference of 14·5. While the difference is but small when mixtures are under examination, the low figure for butter recommends the process.

Polenske's process gives a difference between the titration figures for insoluble volatile fatty acids, which is small, and the determination of the cocoanut-oil is based upon a consideration of the relationship existing between the titration figures for insoluble volatile and soluble volatile fatty acids, and upon the appearance of the acids which distil over. Polenske also works with 5 grms. of fat, The

process is highly empirical, and a special apparatus of standard dimensions is required.

In the process described below, the present authors have succeeded in markedly increasing the difference between the titration figure for the insoluble volatile fatty acids from cocoanut-oil, and the titration figure for the insoluble volatile fatty acids from butter. The process is as follows:—

Three grms. of the filtered fat are saponified in a 300 cc. flask with 10 cc. of absolute alcohol, and 2 cc. of aqueous sodium hydrate (50 grms. per 100 cc.) The alcohol is driven off, the residual soap is dissolved in 50 cc. of boiling water, 10 cc. of concentrated hydrochloric acid is added, and then 50 grms. of anhydrous granulated calcium chloride. The calcium chloride must be added *after* the liberation of the fatty acids by the hydrochloric acid. The flask is then fitted with a cork through which pass two glass tubes. One of these is about 7 mm. in diameter, and is bent at the centre at an angle slightly greater than 90°. The free end of this tube passes through a rubber-stopper which fits into the wide end of an ordinary Liebig condenser. (A Liebig condenser 49 cm. in length is a convenient size). The other glass tube is bent in that length which is inside the flask along the neck and down the concave side of the flask, and is slightly turned up at the tip. The tip is pointing *away* from the condenser, and almost touches the bottom of the flask. The free end of the tube, which is 5 mm. in diameter, is straight, and is connected by a rubber piece to a boiler. The flask is immersed down to the level of the contained liquid in a calcium chloride bath, boiling briskly but not violently at 141—146° C. The flask is inclined in the opposite direction to that which is usual in steam distillations (*i.e.*, with the neck pointing *towards* the condenser) in order to avoid an acute angle in the exit tube. When ebullition commences in the flask the steam from the boiler is turned on, and the steam distillation is proceeded with until 500 cc. of distillate have passed over. The distillate is collected through an ordinary wet English filter into a 500 cc. flask. The passage of the steam must not be so rapid as to cause the free end of the inner condenser tube to become hot. The calcium chloride bath is kept at 141—146° C. by the cautious addition of cold water when required. The distillation occupies from one and a-half to one and three-quarter hours, and requires practically no attention except the occasional addition of water to the chloride bath.

When 500 cc. of distillate have been collected the tube conveying the steam to the flask is quickly disconnected from the boiler, and then the exit tube from the flask is disconnected from the condenser. The liquid in the 500 cc. flask is rejected.

The inner condenser tube is well washed out several times with cold water on to the filter, and the filter and the insoluble acids are then well washed with cold water to remove hydrochloric acid and any soluble fatty acids. All these aqueous washings are rejected. The condenser tube is then washed out with hot methylated spirit into a small flask, and finally the acids on the filter are dissolved out with hot methylated spirit, the solution being added to the alcoholic condenser washings. The solution thus obtained of the insoluble volatile fatty acids is then titrated with N/10 baryta.

The dimensions which have been given for parts of the apparatus employed are set forth as a guide and for the sake of convenience, but, with the exception of the size of the distilling flask, are not to be regarded as rigidly essential. The general arrangement of the parts of the apparatus should, however, be adhered to. The following results were obtained:—

Insoluble Volatile Fatty Acids.

Mean figure for butter, cc. N/10 $Ba(OH)_2$	14·67
Figure from authenticated butter-fat, cc. N/10 $Ba(OH)_2$	15·0
Mean figure for cocoanut-oil, cc. N/10 $Ba(OH)_2$ ..	66

In view of the fact that some butters which were examined gave titration figures by the above process which were rather over 15, and as authenticated butter-fat gave a titration figure higher than that given by some butters, the authors have selected 16 as the "titration standard" for genuine butter. Taking 66 as the "titration standard" for cocoanut-oil, a difference of 50 is obtained. The following results were yielded by mixtures:—

Per cent of cocoanut-oil present.	"Titration figure," cc. N/10 $Ba(OH)_2$ required.	Per cent of cocoanut-oil found.
10*	21·4	10·8
10*	19·7	7·4
15	23·2	14·4
17	25·4	18·8
18	23·4	14·8
20*	26·8	21·6
20*	26·2	20·4
20*	24·8	17·6
25	29·0	26·0
30	30·9	29·8
35 (*a*)	35·7	39·4
35 (*b*)	35·5	39·0

The results which are given in the table have not been specially selected. Those mixtures of the same percentage composition which are marked with an asterisk were made up with different specimens of butter-fat, and are not duplicate results for one and the same mixture. The figures given for the mixture containing 35 per cent cocoanut-oil represent the results of duplicate experiments with the same butter-fat.

The appearance of the fatty acids which distil over is of interest. In the case of butter-fat towards the end of the distillation, the acids coming over are in very bulky woolly-like masses which solidify in the condenser tube and on the filter. The same phenomenon is presented in the case of cocoanut-oil, although not so markedly, at a considerably later stage of distillation. In mixtures of cocoanut-oil and butter-fat the bulk of these solid fatty acids is much reduced.

The calculation of the results is simple. If A represents the titration figure for the insoluble volatile fatty acids obtained, then:—

$(A - 16) \times 2$ = percentage of cocoanut-oil in *fat* taken.

The process is rapid. From beginning to end it requires about two and a-half hours, and during most of that time very little personal attention is called for. The manipulations involved are few in number, and are not complicated or tedious, and the apparatus employed is simple and readily set up.

The authors have under consideration the application of the process to the estimation of cocoanut-oil in admixture with margarine.

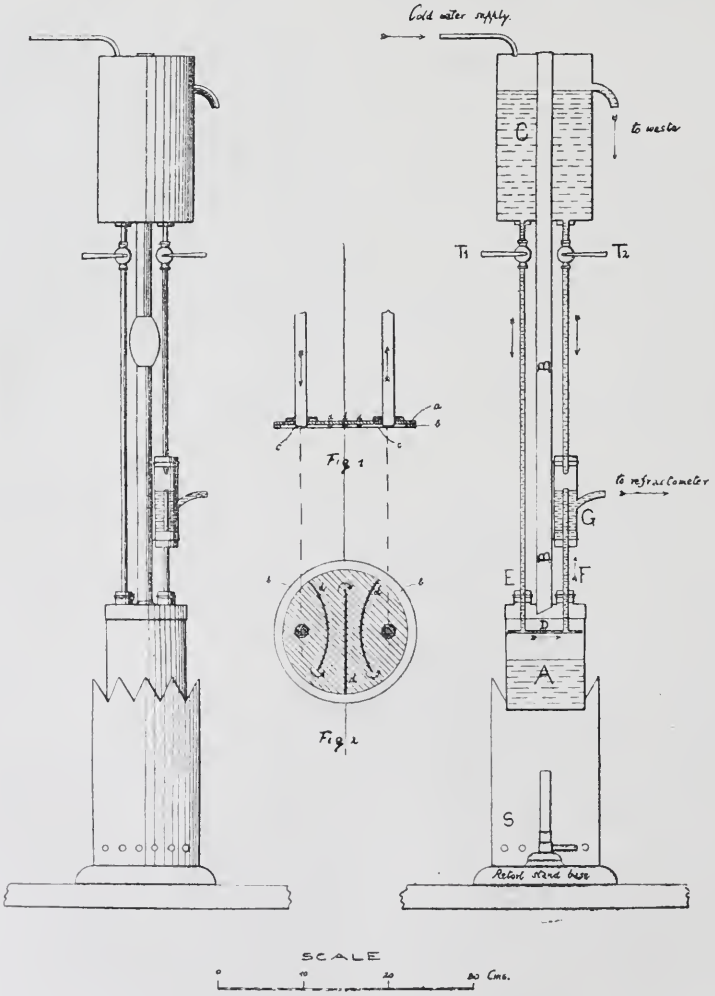
Inks and Forgery.—In the October number of *Knowledge* Mr. Ainsworth Mitchell, who it will be remembered recently gave evidence in a case dealing with a forged will, has a striking article on inks. Incidentally he lets his readers into the secret as to the tests which he applies in order to discover the age of any particular piece of writing. If it is shown that the ink on a document purporting to be drawn up, say, ten years ago, is really quite fresh, then there is every chance that the writing has been forged. An examination of the colour of the ink may be helpful. Blueblack ink may be recognised as fresh up to the sixth day, and in after years its age may be told when the blue provisional pigment has faded and left only the black. The blue colouring as time goes on is hardly acted upon by reagents, but for a year or two it is. In fact, writing done within that time will at once diffuse if treated with a 50 per cent solution of acetic acid, whereas when it is five or six years' old, diffusion, if it takes place at all, is very slow and limited in extent. A still more useful reagent is a saturated solution of oxalic acid, which causes the pigment of relatively fresh writing to give an immediate smudge, but has very little, if any, effect on writing six or eight years old.

AN IMPROVED WATER HEATER FOR THE BUTYRO-REFRACTOMETER.

By CHARLES A HACKMAN, F.I.C.

THE apparatus shown in the accompanying sketch has been designed to meet the want of a heater that—

1. Shall be readily portable.
2. Shall occupy a minimum amount of bench room.
3. Shall be capable of being quickly brought into action when it
   - *a*. Shall deliver a stream of water for an indefinite period heated to a pre-determined constant temperature,
   - *b*. Which temperature may subsequently be raised or lowered in a few seconds, between a range of 60° C. to 25° C. or 20° C., the lower limit depending on the temperature of the cold water supply. This last condition is essential when it is required to use the refractometer at, say, 45° C. for one test, and at 25° C. for another shortly afterwards.



As will be seen from the illustration, the apparatus consists of a copper boiler A, fitted centrally with a copper tube B, which acts both as a condenser and also as support for the constant-level reservoir C. The disc-heater for the refractometer supply is shown suspended in the boiler at D. It is connected to the constant-level reservoir by the small copper tube E, and to the glass mixing-chamber G by the tube F, which tubes, by passing through the openings in the head of the boiler, also serve to support it in position. The construction of the disc-heater (twice-enlarged) is shown in detail in Figs. 1 and 2.

It consists of a circular copper plate, *a*, carrying the inlet and outlet tubes. On the under side of this plate is soldered the ring, *b*, to which in turn is soldered the disc of thin electrolytic copper-foil, *c*. The plate *a* has fixed to it copper-wire strips, *d*, *d*, *d*, as shown in plan in Fig. 2 and in section in Fig. 1. These strips serve to increase the distance through which the water has to flow in its passage as a film over the copper-foil and ensure its becoming adequately heated when steam is generated in the boiler.

The whole apparatus is carried on a retort stand with a base 6 inches by 9 inches, being clamped in position by the central vertical tube (clamp not shown in illustration).

To put the apparatus into action, the burner (protected from draughts by the zinc screen S) is lighted and at the same time the cold water supply is turned on and adjusted so that the water is kept at constant level in the reservoir. As soon as the water in the boiler is in a state of ebullition the flame of the burner is adjusted to keep it vigorously boiling, but not to such an extent as to allow steam to

escape from the top of the condenser tube. Water is now admitted to the disc-heater by opening the cock, T_1, and, supposing it is desired to take a refractometer reading at 40° C., carefully adjusting until the flow of water is sufficiently retarded to indicate a temperature of about 45° C. at the refractometer thermometer. Directly the thermometer is steady, cold water is admitted by the cock T_2—the rate of its entry being at once seen in the glass mixing-chamber. This flow is adjusted until the thermometer indicates 40° C., when the latter will remain at this temperature for as long a period as the apparatus is kept working.

If after this first determination it be now desired to refract an oil, say, at 25° C., this temperature may be quickly attained by increasing the flow through T_2, and again carefully adjusting until the refractometer thermometer indicates the desired point.

The writer has had the apparatus in use in his laboratory for the past month, and found it to answer all requirements perfectly.

RESEARCHES UPON THE COMPLEXITY OF TELLURIUM*

By WILLIAM R. FLINT.

Introductory.

In two papers from the Kent Chemical Laboratory of Yale University a description has been given of a hydrolytic method for the fractionation of tellurium (Browning and Flint, *Am. Journ. Sci.*, xxviii., 112 and 347). An account also has been given, in the second paper, of results obtained from a preliminary application of the process, in which it was indicated not only that the substance might really be complex in spite of the almost conclusively negative evidence hitherto adduced, but also that its anomalous position in the periodic system might be due to the actual presence, as Mendeleeff predicted, of a constituent having a higher atomic weight.

In the work referred to, the fractionation was so conducted as to produce both end fractions simultaneously, and since the method employed was practically that of fractional crystallisation, this involved, unless the operation had been long enough continued, the introduction into each of these portions of material from the middle fractions.

It was therefore determined to modify the fractioning process in such a way as to secure a more rapid separation of each end fraction independently, and to apply it to a much larger amount of material.

Preparation of Material.

About 1 kilogrm. of crude tellurium dioxide, extracted by hydrochloric acid from electrolytic copper residues, supplied by the Baltimore Copper Smelting and Rolling Co., was treated by the same purification processes as those described in the papers cited, the distillation and re-distillation, in hydrogen, being performed in this case in a silica tube, from porcelain boats. The tube was very carefully cleaned between the distillations, and, in re-distilling, fresh boats were used.

Plan of the Investigation.

From the method of fractioning adopted, the investigation naturally divides into two parts, in the first of which will be described (1) determinations of the atomic weight of the tellurium in unfractionated material; and (2) the preparation by hydrolysis with water of a series of fractions, together with atomic weight estimations made upon the tellurium in them. In the second part will be given an account of an experiment upon a fractionation by nitric acid, and of a preliminary investigation of the less easily hydrolysed fraction.

* From the *American Journal of Science*, xxx., p. 209.

Part I.

As a check upon the whole work 150 grms. of the purified product were dissolved in nitric acid (sp. gr. 1·25) and crystallised out as basic nitrate by evaporation of the solution at about 85° C. After being washed with concentrated nitric acid, the basic nitrate was dried by heating at 110° to 120° C. in specially constructed electric drying ovens, through which was passed a current of air dried by sulphuric acid. The air was bubbled first through a solution of potassium hydroxide, then through concentrated sulphuric acid, and finally filtered by passing through a tower containing cotton-wool.

Portions of this preparation were then weighed out in platinum and brought to constant weight by heating, for periods of about twelve hours each, at 140° C. in air dried as just stated, in the electric heaters. The temperature was next raised, and the nitric acid expelled from the compound by ignition up to 425° to 450° for twenty to twenty-four hours. The experiments were finally completed by a short ignition over a Bunsen burner at such a temperature as would ensure a glassy condition of the fused dioxide.

In all the basic nitrate experiments detailed in this paper, the weighings were made by the method of oscillations, a standardised set of weights employed, and a correction for the inequality of the balance arms applied. Lastly, the weights were reduced to a vacuum. The corrected results of the determinations made upon the unfractionated material, which, excepting No. 5, were performed in pairs, are given in Table I. It should be added that in no case was there evidence of the escape of traces of dioxide by volatilisation.

Table I.—*Unfractionated Material.*

Exp.	$2TeO_2.HNO_3$ taken. Grms.	$2TeO_2$ found. Grms.	Atomic weight of tellurium.
1.. ..	4·26930	3·56471	127·41
2.. ..	3·66863	3·06339	127·48
3.. ..	3·17350	2·64983	127·46
4.. ..	3·43498	2·86827	127·48
5.. ..	5·47269	4·56963	127·44
	20·01910	16·71583	Mean 127·45

It may be noted that the mean atomic weight, 127·45, is practically identical with that found by Norris (*Journ. Am. Chem. Soc.*, xxviii., 1675), and that the concordance of these experiments is quite as good as those given by him. The close agreement of this result with both the figure given by Norris and also those found by numerous other investigators indicates a complete correspondence in quality between the material employed in the present research and that used by others. It also confirms the general conclusion that the atomic weight of tellurium, when prepared by the ordinary methods, is 127·5.

The Fractionation by Water Hydrolysis, and Atomic Weights of the Fractions Obtained.

(See accompanying plan).

Five hundred grms. more of the re-distilled tellurium were oxidised by nitric acid and converted to tetrachloride by repeated evaporation with hydrochloric acid. The solution, containing as little excess of acid as possible, was, in four portions, diluted with about 4 litres each of boiling distilled water, and allowed to cool. The white crystalline dioxide which separated out was collected on a filter and washed. After solution in hydrochloric acid (in slight excess) it was re-precipitated by abundant dilution as before. When the fourth repetition of this process had been made, using in each case only the dioxide which had been previously precipitated by dilution, a small portion of the fourth precipitate was taken out as a sample. This was crystallised from nitric acid by the usual method, and a second series of basic nitrate experiments, conducted in every way like those of Table I., was performed. The data of these are found in Table II.

TABLE II.—*After Four Fractionations.*

Exp.	$2TeO_2.HNO_3$ taken. Grms.	$2TeO_2$ found. Grms.	Atomic weight of tellurium.
1.. ..	3·07931	2·56876	126·53
2.. ..	2·73622	2·28276	126·62
3.. ..	2·36328	1·97153	126·57
4.. ..	2·08497	1·73948	126·64
	10·26378	9·56253	Mean 126·59

The fractionation process was continued with the remainder of the fourth precipitate in the same manner as before, and the operations repeated without change until ten fractionations had been performed. By heating to boiling the filtrate from the eighth precipitate a further separation of dioxide was obtained from this liquid, and boiling for ten or fifteen minutes threw out about 42 grms. Part of this sample was converted to basic nitrate and subjected to the same process of analysis as the previous preparations, the results being recorded in Table III.

TABLE III.—*After Eight Fractionations.*

(From Filtrate).

Exp.	$2TeO_2.HNO_3$ taken. Grms.	$2TeO_2$ found. Grms.	Atomic weight of tellurium.
1.. ..	2·12253	1·76842	125·36
2.. ..	2·51320	2·09413	125·45
3.. ..	3·76225	3·13447	125·32
4.. ..	3·88080	3·23336	125·36
	12·27878	10·23038	Mean 125·37

Fraction ten consisted of but 23 grms. of dioxide. Since the fractioning process had reduced the quantity of dioxide from over 600 grms. to a little more than 20, it seemed possible that the limit might have been reached. About 15 grms. were consequently transformed to basic nitrate, in two separate preparations. The purpose of this was to eliminate, if possible, the objection that this lowering of the atomic weight might be due to lack of constancy of composition of the basic nitrate. The first sample, the data of whose analysis by the basic nitrate method (applied exactly as described for the preceding preparations) are given in experiments 1 and 2 of Table IV., contained about 5 grms.; the second, experiments 3 to 7, 16 grms.

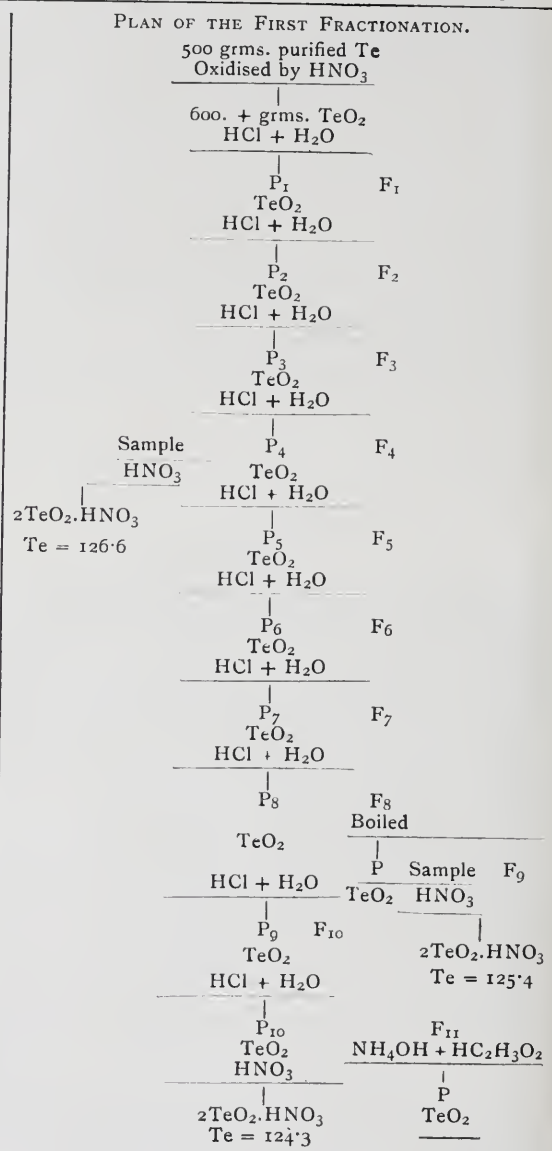
TABLE IV.—*After Ten Fractionations.*

Exp.	$2TeO_2.HNO_3$ taken. Grms.	$2TeO_2$ found. Grms.	Atomic weight of tellurium.
1.. ..	2·06311	1·71688	124·25
2.. ..	2·18903	1·82172	124·27
3.. ..	3·56161	2·96446	124·42
4.. ..	2·99821	2·49537	124·37
5.. ..	2·86977	2·38824	124·27
6.. ..	2·47403	2·05898	124·31
7.. ..	4·85363	4·03943	124·32
	21·00939	17·48508	Mean 124·32

The concordance of these results is sufficiently close to indicate that the two preparations of fraction ten were practically constant in composition. Experiment 7 in the above table was performed in parallel with Experiment 5 of Table I.

A comparison of the mean values given in the four preceding tables shows a remarkable lowering of the atomic weight with the progress of the fractionation. In considering the difference between the mean result, 124·3, of Table IV., and that, 125·4, of Table III., it should be noted that, since the material which gave the latter figure was derived from the filtrate of fraction eight, it was to have been expected that its atomic weight would be higher than that of fraction eight itself. Owing to the small quantity remaining of fraction ten, it was impossible to make another direct fractionation. But the dioxide produced in the experiments of Table IV. was dissolved in hydrochloric acid and the hydrolysis repeated once more,

PLAN OF THE FIRST FRACTIONATION.


500 grms. purified Te
Oxidised by HNO3
600. + grms. TeO2
HCl + H2O
P1 TeO2 HCl + H2O F1
P2 TeO2 HCl + H2O F2
P3 TeO2 HCl + H2O F3
Sample HNO3
2TeO2.HNO3 Te = 126·6
P4 TeO2 HCl + H2O F4
P5 TeO2 HCl + H2O F5
P6 TeO2 HCl + H2O F6
P7 TeO2 HCl + H2O F7
P8 TeO2 HCl + H2O F8
Boiled
P TeO2 Sample HNO3 F9
2TeO2.HNO3 Te = 125·4
P9 TeO2 HCl + H2O F10
P10 TeO2 HNO3
2TeO2.HNO3 Te = 124·3
F11 NH4OH + HC2H3O2
P TeO2

the precipitate being converted to basic nitrate. The basic nitrate experiments gave 124·62 and 124·64, but these figures cannot be accepted as conclusive. In the first place, they were made upon material which had already been used for previous determinations, in which the dioxide formed had been heated in platinum up to fusion. During the course of the basic nitrate experiments described in this paper, a progressive, but minute, loss of weight was observed in the platinum crucibles used. This fact suggests the possibility that the tellurium may have become contaminated with a little platinum, which would of course raise the atomic weight found in these two experiments. And second, while these two experiments were in progress, an extreme humidity unfortunately characterised the weather. The tendency of this condition would be to increase the atomic weight also, since traces of moisture absorbed by the basic nitrate during those short, but necessary, periods in which it was out of the heaters and desiccator for the purpose of weighing, would tend to

produce hydrolysis to dioxide, and the nitric acid liberated from the compound would be expelled in the next heating. This also would increase the value found for the atomic weight. It is therefore at present impossible to conclude with certainty that the figure 124·3 represents the true atomic weight of the element tellurium, since the value may perhaps lie a little below this number.

Conclusion.

Using the customary methods of purification, a large quantity of tellurium has been prepared. By the basic nitrate process, this has been shown, in five experiments with 20 grms. of material, to have the atomic weight 127·5, generally accepted for tellurium. Repeated hydrolysis with hot water of a solution of 500 grms. of this preparation in hydrochloric acid has furnished, in ten fractionations, a product consisting of 23 grms. of dioxide. The tellurium in this fraction, it has been demonstrated, also by the basic nitrate method in seven experiments, using 21 grms., has an atomic weight of 124·3. Two intermediate fractions, estimated in the same way, give values of 126·6 and 125·4 respectively, these three results taken together exhibiting a progressive diminution of the atomic weight.

In March of the year 1869, Mendeleeff, in announcing the periodic law, made the following statement (*cf. Ber.*, xiii., 1799):—"Die Atomgewichtsgrosse eines Elementes kann bisweilen corrigirt werden, sobald seine Analogein bekannt sind. So muss dass Atomgewicht des Te nicht 128, sondern 123—126 sein." The problem inferentially stated by him, which for the last forty years has supplied the subject-matter of researches too numerous to mention, appears to have been solved, and affirmatively, by the research herein described.

Brauner's various low results which he published in 1899 (*Journ. Chem. Soc.*, lv., 382); Heberlein's value of 126·99 ("Dissert. Basel," 1898); Steiner's of 126·4, obtained in 1901 by fractional distillation of diphenyl tellúride (*Ber.*, xxxiv., 570); Marckwald's of 126·85, in 1907, from fractional crystallisation of telluric acid (*Ber.*, xl., 4730); and the figure 126·53, found in 1909 by Browning and Flint (*loc. cit.*), using hydrolysis with water, have been the chief divergences in the past from the accepted value.

The present investigation has furnished more than 20 grms. of a purified product possessing an atomic weight of 124·3. Since this preparation was extracted from a large quantity of material which is proved by its atomic weight, 127·45, to correspond to what has been hitherto considered elementary substance, the figure 124·3 is apparently the nearest approach which has yet been made to the true atomic weight of the element tellurium.

(To be continued).

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,*

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, &c.

By PERCY H. WALKER.

(Continued from p. 182).

Materials Used for the Manufacture of Cancelling and other Stamping Inks.

1. *Volatility and Penetrating Power.* — The methods which have been described above will be found useful in determining the suitability of liquids for use as bases or constituents of bases of cancelling and other stamping inks.

2. *Sedimentation Test.*—A modification of the sedimentation test described may be employed with good results for the purpose of ascertaining the suitability of lampblack and other pigments for use in the manufacture of cancelling and other stamping inks. The results, of course, are mainly of value for purposes of comparison. The conditions of the test may be modified to suit the purposes of the investigation and the character of the materials to be compared. The writer has obtained good results in the comparison of lampblacks and other blacks rich in uncombined carbon by the following method, which was so planned that the results might be applied to stamping inks made with either a water-solution base or an oil base:—Mix 0·5 grm. of the black to be tested in a mortar with dilute glycerin (87·5 cc. of glycerin diluted with water to 1 litre). Rinse the mixture into a 100 cc. Nessler cylinder and dilute to the 100 cc. mark, using the same dilute glycerin. After having prepared a series of tubes, each containing a portion of one of the blacks to be tested, close each tube with a cork and shake thoroughly each tube successively, performing the operation as quickly as possible in order that the time of settling may be approximately the same in the case of each sample. Allow the cylinders to stand at rest in a place free from jar, and record from time to time the height of the sediment formed by the deposition of the blacks. When submitted to this test, a black which is suitable for the manufacture of a cancelling or stamping ink should occupy a volume of not less than 25 cc. when the sediment has stopped settling.

3. *Ash, &c.*—Blacks, dyes, and other substances used for the manufacture of cancelling and other stamping inks should be carefully examined to insure the absence of considerable percentages of substances which are not essential to the production of an ink of good quality. It can generally be assumed that the presence of considerable quantities of any substance which does not actually contribute to the desirable qualities of the ink will detract therefrom. Black pigments rich in carbon of high specific gravity due to the presence of a large percentage of ash are highly unsuitable for the manufacture of stamping inks. Only the concentrated brands of coal-tar dyes should be used, unless the substances with which the less concentrated are diluted have been found to actually contribute to the working qualities of the ink to be produced.

Babbitt Metal (*Rapid Analysis*) (Walker and Whitman, *Journ. Ind. Eng. Chem.*, 1909, i., 519).

1. *Copper.*—Weigh 1 grm. of the alloy into a 250 cc. beaker, add 20 cc. of hydrochloric acid and 5 cc. of water, heat, and complete the solution by adding nitric acid in small amounts; with most alloys solution can be effected in a very few minutes and without adding more than 1 or 2 cc. of nitric acid. Evaporate off the acid on a steam-bath. It is not necessary to carry to complete dryness, but practically all the acid should be driven off and the residue should be pasty. Add 25 cc. of a solution made of 200 grms. of tartaric acid and 260 grms. of potassium hydroxide, the whole being made up to 500 cc. with water. Heat on the steam-bath until solution is completed, add 25 cc. of water, boil, add 25 cc. of a 0·2 per cent invert sugar solution, boil for two minutes, filter through asbestos, wash the precipitate of cuprous oxide with water, dissolve in nitric acid, catching the copper solution in a 200 cc. flask, and determine copper by any good volumetric method. Equally good results can be obtained by following Low's iodide method (*Journ. Am. Chem. Soc.*, 1902, xxiv., 1082), or Jamieson, Levy, and Wells's thiocyanate and iodate method (*Journ. Am. Chem. Soc.*, 1908, xxx., 760). The results are uniformly a little low. This error is not due to the volumetric methods employed, both of which give exceedingly accurate results, but to the fact that nearly 6 per cent of the copper present is not precipitated as cuprous oxide. This loss is uniform, for if we add 6 per cent of the copper determined, the result will be the per cent of copper in the alloy. The statement is frequently made that if a babbitt metal is decomposed by nitric acid, evaporated to dryness, taken up with nitric acid and filtered, copper can be determined in the filtrate with an error of not more than one or two tenths of 1 per cent. This is not the case, as the error with an alloy containing 5 per cent of copper will frequently be from 0·5 to

* *Bulletin* No. 109, Revised, U.S. Department of Agriculture, Bureau of Chemistry.

0·7 per cent, while by the method just described without correction the error will be less than 0·3 per cent, and by applying the correction this error is removed entirely.

2. *Lead.*—Dissolve 0·5 to 1 grm. of alloy in a 250 cc. beaker as in the determination of copper; when solution is complete evaporate to dryness on the steam-bath, add 5 cc. of strong hydrochloric acid (with as much as 10 per cent of antimony use 10 cc. of hydrochloric acid), warm for a few minutes, remove from steam-table, add, with stirring, 150 cc. of 95 per cent alcohol, let stand at room temperature for two hours, filter on a Gooch crucible, and wash with 95 per cent alcohol, using about 100 cc. Suck as dry as possible, dry crucible in an air-bath (one hour at 105° C. is sufficient, though the lead chloride can be heated at 150° with perfect safety). Weigh as lead chloride, add 0·0085 grm. to the weight of the precipitate, and multiply by 0·74473; the product gives the weight of lead.

3. *Antimony.*—Antimony is determined by W. H. Low's method (*Journ. Am. Chem. Soc.*, 1907, xxix., 66) slightly modified as follows:—To 1 grm. of alloy in a 450 cc. Erlenmeyer flask add 10 to 15 cc. of strong sulphuric acid, and heat on a hot plate until the alloy is thoroughly decomposed. This is generally accomplished in about thirty minutes from the time fumes of sulphur trioxide begin to be given off. Cool, add 200 cc. of water and 20 cc. of strong hydrochloric acid, boil to make sure that all sulphur dioxide is driven off, cool and titrate rapidly with potassium permanganate which has been standardised against metallic antimony. The true end-point is found when a pink colour shows after agitating the liquid, though this pink will very soon disappear. The only change made in the Low method of procedure is to add somewhat less hydrochloric acid. The results are sufficiently accurate for commercial purposes, but the tendency is to get results 0·3 to 0·4 per cent high.

4. *Tin.*—Tin is also worked by W. H. Low's method (*Journ. Am. Chem. Soc.*, 1907, xxix., 66), except that it seems to be more satisfactory to use a separate portion of the alloy and reduce with steel turnings instead of with metallic antimony. Treat from 0·2 to 1 grm. of alloy (do not use an amount of alloy containing more than 0·2 grm. of tin) in a 450 cc. Erlenmeyer flask with 10 to 15 cc. of strong sulphuric acid, heat on the hot plate until the alloy is thoroughly decomposed, cool, add 200 cc. of water, 30 cc. of strong hydrochloric acid, and about 1 grm. of steel turnings, heat, and when reduction appears complete, but before the last particles of steel have dissolved, place a two-hole rubber stopper in the neck of the Erlenmeyer flask—one hole of the stopper should carry a tube reaching below the surface of the liquid, the other hole should carry the short arm of a bent tube, the long arm of which reaches nearly to the bottom of a 100 cc. Erlenmeyer flask containing a solution sodium bicarbonate. This small Erlenmeyer is held on the bent tube by a cork which has a notch cut in it to act as a vent. Through the tube reaching below the surface of the liquid in the large Erlenmeyer pass a current of carbon dioxide, heat to boiling until all steel is dissolved, continue passing carbon dioxide, and cool as quickly as possible; loosen the stopper but let the current of carbon dioxide continue; add cautiously some starch solution and titrate with tenth-normal iodine. It is necessary to absolutely exclude air and to standardise the iodine solution with pure tin.

Glue.

Chemical analysis gives little information in regard to the value of glue. The chemical determinations are of more use in deciding as to whether a delivery is the same as a sample submitted than in deciding which is the best of a series of samples. Fernbach ("Glues and Gelatine," p. 4) says, "Save for alkalinity or acidity, the chemical properties of glue are not factors in rational systems of test." In determining whether specifications have been complied with in making inking pads chemical tests are often of use.

1. *Moisture.*—Heat 3 grms. of the finely divided sample for two hours in an oven at 105° to 110° C. It is important to use about the same quantity each time. Fernbach states that a good glue should contain not less than 8 or more than 16 per cent of moisture.

2. *Ash.*—The sample used for the moisture determination may be ashed. Ignite in porcelain or quartz, do not use platinum. Care is necessary in the ignition, which should be carried out at as low a temperature as possible. The ash should vary from 1·5 to 3 per cent. The condition of the ash gives some clue as to the origin of the glue. If the ash fuses, gives a neutral reaction, and contains traces of phosphates and chlorine, it indicates a bone glue. The ash of a hide glue does not fuse, is slightly alkaline, and does not contain chlorides and phosphates ("Glues and Gelatine," p. 59).

3. *Reaction.*—Test the solution in water with litmus-paper. A quantitative determination is seldom of use ("Glues and Gelatin," p. 61).

4. *Gelatin.*—A satisfactory approximation of the gelatin content is obtained by determining the nitrogen and multiplying by 5·56.

5. *Water Absorption.*—Place 10 grms. of the sample, preferably in sheet form, in a weighed 400 cc. beaker, pour 200 cc. of water at 15° C. on the glue, cover the beaker, and let it stand for twenty-four hours in a refrigerator at a temperature from 14° to 18° C. Then pour off the water and weigh the remainder. With ground glue some difficulty may be experienced in decanting the water; this is sometimes avoided by using a cage of fine wire gauze or a piece of blotting cloth to hold the ground glue. The temperature at which the water absorption is determined may be varied, but the figures obtained at one temperature are not to be compared with those at another. The determination cannot be carried out on most glues at temperatures much above 20° C.

6. *Viscosity.*—Soak 50 grms. of glue in 250 cc. of water (at 20° C.) over night. Then dissolve by warming, not over 60° C., transfer to a 500 cc. flask, dilute to the mark at 30° C., strain through bolting cloth into a somewhat larger flask, heat to 60° C., cool to 30° C., and determine the viscosity immediately by the Engler-Ubbelohde method at 30° C. (The Bureau of Chemistry instrument requires 51·4 seconds to empty 200 cc. water at 20°). Concordant results cannot be obtained by running the same solution a second time through the viscosimeter, the solution flowing faster each time. Fairly good results, however, can be obtained by heating the solution again to 60° C. and cooling to 30°. When the size of the sample will permit, make up enough solution to run duplicates.

7. *Jelly Strength.*—This is one of the most important tests. Fernbach states that no apparatus gives as reliable results as the simple testing of the jelly by the finger. This, however, is an unsatisfactory method when only occasional samples of glue are examined. Weigh 50 grms. of glue and 250 grms. of water into a 600 cc. beaker, allow to stand at room temperature for thirty minutes, then heat in a water-bath at 60° C. until dissolved, add 250 grms. of water at 60° C., making a total of 500 grms. of water. Mix the solution, and pour 150 cc. into a glass and cool for one and one-half hours with cracked ice. While still in the ice determine the strength by the shot test as formulated by Lipowitz and modified by Fernbach (Fernbach, "Glues and Gelatine," p. 46).

8. *Melting-point of Jelly.*—This determination is best made according to Cambon's fusiometer method (Küttner and Ulrich, *Zts. öff. Chem.*, 1907, xiii., 121). The apparatus used in the Bureau of Chemistry is only a very slight modification of Cambon's, and consists of a metal cup (a ferrule) 22 mm. high, 17 mm. in diameter at the top, and 15 mm. in diameter at the bottom, weighing 7 grms., and a glass tube 9 mm. in diameter, and 160 mm. long, with the lower end sealed. Weigh accurately 2 grms. of glue, place in a test-tube with exactly 8 cc. of water, cork, and allow to stand over night. Then dissolve the glue by holding the tube in warm water, not over 60° C. By shaking the tube a homogeneous liquid is easily obtained.

Place the metal cup on a horizontal surface, suspend the glass tube vertically at about the centre of the cup, with the closed end approximately 1 mm. above the bottom. Pour the glue solution into the cup and allow it to set. (This may be hastened by surrounding the cup with ice-water). Fill a 600 cc. Jena beaker, 12 cm. high and 9 cm. in diameter, two-thirds full of water at 15° C., and set it in a pan of water at 40° to 42° C. The water level in the pan should be about 15 mm. below that in the beaker. Clamp the glass tube in a vertical position at such a distance above the centre of the beaker that the metal cup is submerged to about 1 mm. from the top. Suspend a centigrade thermometer, graduated in tenths, close to the cup, and note the temperature at which the cup drops. Good glues have a melting-point above 30° C., while that of inferior grades is several degrees lower.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cli., No. 7, August 16, 1910.

Energy of Radium Rays.—William Duane.—The author has tried five different methods to determine the energy of radium rays. The bolometer, radiometer, and thermoelectric pile gave no results, but positive results were obtained with a differential thermometer and a sensitive calorimeter. The α-rays of radium C set free a certain amount of heat which is a measure of the energy of the rays.

Photochemical Decomposition of Alcohols, Aldehydes, Acids, and Ketones.—Daniel Berthelot and Henry Gaudechon.—The ultra-violet rays bring about decompositions which are as deep seated as those produced by electrolysis or fermentation, and there are certain resemblances between the three processes. Photochemical decomposition gives the same products with pure substances and their aqueous solutions. In organic compounds RX with function X two radicles R unite as in electrolysis. The alcoholic group CH_2OH gives H_2, OH, and C, which react to give CO and H_2O. The aldehyde group COH gives CO and H. The acid group CO_2H gives large quantities of CO_2, some CO, and H_2.

No. 8, August 22, 1910.

Catalytic Preparation of Oxyphenols and Diphenylene Oxides.—Paul Sabatier and A. Mailhe.—Mixed oxides of alcohols and phenols may be prepared by the catalytic dehydration of phenols by means of ThO_2.

$$2(C_6H_5.OH) + ThO_2 = H_2O + ThO(OC_6H_5)_2$$
$$ThO.(OC_6H_5)_2 = ThO_2 + (C_6H_5)_2O.$$

When the temperature is raised dehydrogenation follows, and diphenylene oxides, *e.g.*, $\begin{matrix} C_6H_4 \\ | \quad \rangle O \\ C_6H_4 \end{matrix}$, and its homologues are formed.

No. 9, August 29, 1910.

Exact Atomic Weights of Oxygen and Silver.—G. D. Hinrichs.—The author has analysed the results obtained in 656 determinations of the atomic weights of oxygen and silver, performed during the century 1810—1910. The results differ from 16 and 108 respectively by 100-thousandths in 7 per cent of the total number of experiments; 50 per cent of the differences are below 0·01 and 70 per cent below 0·02. Undoubtedly the absolute atomic weights are the true atomic weights.

Ethylenic Cyclic Compounds with Ether Oxide Function and their Bromine Derivatives. — M. Busignies.—By the action of methyl and ethyl iodide and benzyl chloride on *p*-ethoxybenzophenone the author has obtained *p*-ethoxydiphenylethylene, fusing at 71°, *p*-ethoxydiphenylpropene, fusing at 54°, and *p*-ethoxyphenylstilbene, fusing at 93°. When bromine acts on these compounds it is found that if the group $CH_2—C<$ is present a dibrom derivative is obtained in the cold. If the group $—CH=C<$ is present, a monobrom derivative is formed and hydrobromic acid is liberated in the cold, while a dibrom derivative is obtained on heating, hydrobromic acid again being liberated.

Zeitschrift für Anorganische Chemie.
Vol. lxvii., No. 2, 1910.

Mutual Conversion of Ortho-, Pyro-, and Meta-phosphoric Acids into one another on Heating.—D. Balareff.—When the vapour tension of the water over heated orthophosphoric acid is increased, the temperature of formation of the pyro-acid rises more quickly than that of the meta-acid. On account of the volatility of the meta-acid the transformation could be investigated only at o relatively low temperatnre, so that it was not possible ta reach the point at which the temperature of formation curves for the pyro- and meta-acids cut one another; *i.e.*, the direct conversion of ortho- into meta-acid could not be effected.

Supplement to the Article on Ferric Acetates (*Zeit. Anorg. Chem.*, 1910, lxvi., 157).—R. F. Weinland and Ernst Gusmann.—By evaporating a concentrated solution of one molecule of ferric chloride and three molecules of sodium acetate, a crystalline ferric acetate can be obtained. The concentrated aqueous solution of the salt gives with sodium platinum chloride the characteristic chloroplatinate of the hexa-acetatotriferric base. The salt is a compound of one molecule of the mono- and bi-acetates of this base.

No. 3.

Atomic Weight of Vanadium II.—Wilhelm Prandtl and Benno Bleyer.—In an earlier series of experiments in which the amount of chlorine in vanadium oxytrichloride was determined, the mean result obtained was 61·3348 ± 0·0087, which gives for the atomic weight of vanadium 51·061 ± 0·024. The reduction of the pentoxide to the trioxide gives a decidedly higher value for the atomic weight, viz., 51·374 ± 0·033, which agrees very well with that given by Roscoe, 51·371 ± 0·066. The difference may be explained by supposing that the trioxide contained traces of higher oxide. The authors consider that little reliance is to be placed upon the results obtained in the reduction of the oxide, as the method is not very accurate.

Theory of the Manufacture of Thorium Salts.—I. Koppel and H. Holtkamp.—The raw material used in the manufacture of thorium is monazite, a phosphate of the rare earths, containing about 60 per cent of rare earths and 5 per cent of ThO_2. It is opened up by heating with concentrated sulphuric acid, and the mixture of the sulphates of the rare earths thus obtained is dissolved in a large quantity of water. Oxalic acid was formerly used to separate the thorium, but it is now found better to neutralise the filtrate from the sulphates, when thorium phosphate is precipitated first while the other earths remain in solution. The thorium phosphate thus obtained contains cerium and didymium; to purify it it is washed, dissolved in hydrochloric acid, and the thorium is precipitated with oxalic acid. The raw thorium oxalate is then decomposed with soda solution. The hydroxide thus obtained is converted into sulphate, and again into hydroxide in order to remove the last traces of impurity. Finally, the hydroxide is dissolved in nitric acid, and the solution is evaporated, and thus the pure nitrate is obtained, The authors have subjected this "sulphate purification

process" to a thorough investigation, in the course of which they determined the solubility of the hydrates of thorium sulphate in sulphuric, hydrochloric, and nitric acids, and have found that the presence of phosphoric acid hinders the separation of sulphate, and when large quantities are present no sulphate precipitate is formed. When the hydroxide which is to be converted into sulphate is dissolved, only hydrochloric acid is used technically, and from the results of the solubility experiments the authors conclude that the use of nitric acid would not increase the yield of sulphate. There would be no harm in having excess of acid, although this is most carefully avoided in the technical process. With a great excess of sulphuric acid the solubility is decidedly decreased, and thus the yield is increased, but then a strongly acid mother-liquor is obtained, and this is difficult to work up. If, however, phosphoric acid is present in the thorium its solvent action is diminished by the excess of sulphuric acid, which is a great advantage. In order to prevent the formation of the gelatinous 4-hydrate, which is difficult to filter, and to obtain the 8-hydrate, the temperature during precipitation must be kept below 42°. In presence of large excess of acid the formation of the 4-hydrate occurs at a lower temperature than in neutral solution.

Heat of Hydration and Vapour-pressure of Thorium Sulphate Hydrates.—I. Koppel.—The author gives tables showing the vapour-pressure of $Th(SO_4)_2.8H_2O$ at 30° and 42°, and the heat of hydration at different concentrations and temperatures.

Lead Coulombmeter, I.—Franz Fischer and Karl Thiele.—Solutions of the lead salts of boron, aluminium, silicon, titanium, zirconium, tin, arsenic, and antimony fluoric acids were prepared and tested to see whether they could be used in a lead coulombmeter. It was found that the only ones that are applicable are lead boron fluoride, lead silicon fluoride, lead zirconium fluoride, and lead tin fluoride. A method of separating tin and antimony may be based upon the formation of complexes of tin disulphide and hydrochloric acid, from which the tin is not precipitated with sulphuretted hydrogen. The mixture of salts is oxidised, and then SnS_2 and Sb_2S_5 are precipitated with sulphuretted hydrogen. The mixed sulphides are dissolved in hydrofluoric acid, and sulphuretted hydrogen is led through the solution. The antimony is then precipitated in the form of the red-brown sulphide. Concentrated sulphuric acid is added to the filtrate, and the hydrofluoric acid is driven off by evaporation. The residue is taken up with water, and sulphuretted hydrogen is led through the solution, when yellow tin disulphide is precipitated.

Use of Potassium Ferricyanide in Alkaline Solution for the Determination of Arsenic, Antimony, and Tin.—Howard E. Palmer.—The method depends upon the oxidation of the oxides by means of potassium ferricyanide in alkaline solution, the equations being :—

$$As_2O_3 + 4K_3Fe(CN)_6 + 4KOH = As_2O_5 + 4K_4Fe(CN)_6 + 2H_2O,$$

$$Sb_2O_3 + 4K_3Fe(CN)_6 + 4KOH = Sb_2O_3 + 4K_4Fe(CN)_6 + 2H_2O$$

$$SnO + 2K_3Fe(CN)_6 + 2KOH = SnO_2 + 2K_4Fe(CN)_6 + H_2O.$$

The ferrocyanide formed is then titrated with permanganate:

$$10K_4Fe(CN)_6 + 2KMnO_4 + 8H_2SO_4 = 10K_3Fe(CN)_6 + 6K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Iodometric Determination of Potassium Ferro- and Ferricyanide.—Werner Mecklenburg.—The method of determining potassium ferricyanide depends upon the oxidation of potassium iodide by the ferricyanide and the volumetric estimation of the iodine liberated by means of thiosulphate. The author has investigated and reports upon the conditions in which satisfactory results can be obtained. The same method can be used for the indirect estimation of the ferrocyanide. The latter can also be estimated by oxidising it with excess of 1/10N permanganate, and determining the excess of permanganate iodometrically. By a combination of the two methods the percentage composition of a mixture of ferro- and ferricyanide can be determined.

Lead Coulombmeter, II.—Franz Fischer, Karl Thiele, and Edward B. Maxted.—The authors describe a method of drying and weighing electrolytically precipitated lead on platinum without previous oxidation, and a titrimetric method of determining lead in presence of an oxidising or reducing acid. With boron fluoric acid, silicon fluoric acid, and *p*-phenolsulphuric acid as electrolyte, the connection between the amount of lead separated, the amount of free acid present, the concentration, and the temperature was determined. The addition of 0·1 to 1 grm. per litre of colloidal substance to the electrolytes does not affect the accuracy of the lead coulombmeter, but 1 grm. per litre of colloid completely prevents the precipitation of lead. The best coulombmeter is obtained by using lead boron fluoride. It may be used with currents from 0·14 to 14 ampère per sq. d.c.m.

Action of Ammonia on Mercurous Chloride.—Haridas Saha and Kumud Nath Choudhuri.—The black substance obtained by the action of ammonia solution on mercurous chloride appears to be a mixture of mercury and white precipitate. Infusible white precipitate, when freshly prepared, is soluble in concentrated ammonia, and if this solution is slowly evaporated over concentrated sulphuric acid *in vacuo* it crystallises out.

Use of Silver in the Determination of Molybdenum, Vanadium, Selenium, and Tellurium.—Claude C. Perkins.—Molybdenum, vanadium, selenium, and tellurium can be determined gravimetrically by allowing their oxides to liberate iodine from potassium iodide in acid solution, and determining the iodine set free by making it combine with specially prepared silver.

Influence of Electrolytes on Solubility.—W. Herz.—The solubility of barium chloride is increased by the presence of alkali chloride. Lithium chloride has the greatest effect, and the other chlorides follow in the order: NaCl, KCl, RbCl. Sodium chloride, potassium chloride, and rubidium chloride increase the solubility of copper sulphate, while lithium chloride lowers it.

MEETINGS FOR THE WEEK.

WEDNESDAY, 19th.—Microscopical, 8. "Hicksonella, a New Gorgonellid Genus," by J. J. Simpson. "Resolution of New Detail in a *Coscinodiscus asteromphalus*" and "A Micrometric Difficulty," by E. M. Nelson. Exhibition of Pond Life.

THURSDAY, 20th.—Chemical, 8.30. "Structure of Xanthonium and Acridinium Salts," by J. T. Hewitt and F. B. Thole. "Application of Viscosimetry to the Measurement of the Rate of Reaction," by A. E. Dunstan. "Iodoacenaphthene," by H. Crompton and Miss M. K. Harrison. "Improved Form of Extraction Apparatus," by J. M. Sanders. "Another Method for Preparing Cuprous Iodide," by A. Harvey. "Constitution of Eriodictyol, of Homoeriodictyol, and of Hesperitin," by F. Tutin. "Synthesis of 3 : 4 : 2′ : 4′ : 6′-Pentamethoxybenzylideneacetophenone, a Methyl Derivative of Eriodictyol, Homoeriodictyol, and Hesperitin," by F. Tutin and F. W. Caton. "Synthesis of Nitrognoscopine and Allied Substances," by E. Hope and R. Robinson. "Aniline Black and Allied Compounds," by A. G. Green and A. E. Woodhead. "Constitution of Coumarinic Acid," by A. Clayton. "Colour Changes of Methyl-orange and Methyl-red in Acid Solution" and "Hydrolysis of Aniline Salts measured Colorimetrically," by H. T. Tizard. "Reduction of Chloric Acid," by R. R. Enfield. "Dynamics of the Decomposition of Persulphuric Acid and its Salts in Aqueous Solution," by Miss L. Green and O. Masson. "Extreme Methylation by Methyl Sulphate," by R. Meldola. "Study of the Dissociation of the Salts of Hydroxylamine in Aqueous Solution," by E. Barrett.

THE CHEMICAL NEWS.

Vol. CII., No. 2656.

ANNUAL REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS, 1911.*

In the autumn of 1909 the Council of the Chemical Society of London voted unanimously in favour of issuing the annual report of the International Committee on Atomic Weights in September or October instead of in January, as heretofore. In that proposition the Chemical Society of France has concurred, and American sentiment has also been favourable to the suggested change. Therefore the change is now made.

The reasons offered for the new policy are very simple:—First, the school year, at least in most educational institutions, begins in the autumn. It is desirable that teachers should then have the latest table of atomic weights at their command, in order to avoid changes after school work has begun. Secondly, publishers of text-books are accustomed to issue their new works in the autumn, and often request early information as to changes which are likely to be made. The proposed change in the time of issuing the table is therefore an aid to teachers, students, and publishers, and no disadvantage to anyone else. The immediate usefulness of the table is increased, and to attain that end should be a main purpose of the Committee.

Since the preparation of the report for 1910, a number of important memoirs upon atomic weights have appeared. The results obtained are, in brief, as follows:—

Chlorine.—The density, composition by volume, and compressibility of hydrochloric acid have been measured by Gray and Burt with great care (*Journ. Chem. Soc.*, xcv., 1633). From the density and volumetric composition, when H = 1·00762, Cl = 35·459. From the density and compressibility, Cl = 35·461. The mean, 35·460, is the value given in the annual table of atomic weights for the past two or three years.

The density of hydrochloric acid has also been determined by Scheuer (*Zeit. Physik. Chem.*, lxviii., 575). who gives measurements made under varying conditions. His final conclusion, based upon his own work after comparison with that of Gray and Burt, is that Cl = 35·466.

Lithium.—Richards and Willard (*Journ. Am. Chem. Soc.*, xxxii., 4), in their important research upon the atomic weight of lithium, measured three distinct ratios; namely, silver to lithium chloride, silver chloride to lithium chloride, and lithium perchlorate to lithium chloride. From these ratios, without the intervention of any others, the following independent values for three atomic weights are obtained:—

Li	=	6·939
Cl	=	35·454
Ag	=	107·871

The value for silver varies from the accepted value, 107·88, by about 1 part in 12000, which is probably less than the actual uncertainty. That for chlorine diverges more widely; namely, by about 1 part in 6000. The new figures are undoubtedly entitled to great weight, but in view of the excellent work done by others it would be unwise to make any hasty change in the table. For lithium, however, the value 6·94 may be taken, replacing the old 7·00.

Strontium.—Thorpe and Francis (*Proc. Roy. Soc.*, A, lxxxiii., 277), in their determinations of the atomic weight

* From the *Journal of the American Chemical Society*, xxxii., No. 10.

International Atomic Weights. (1911).

	Symbol.	Atomic weight.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·09
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·4
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	3·99
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·85
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	6·94
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·07
Tantalum	Ta	181·0
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·4
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0

	Symbol.	Atomic weight.
Uranium	U	238·5
Vanadium	V	51·06
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Yt	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

of strontium, measured six ratios, and obtained the following results :—

Ratio.	Sr =
2Ag to $SrBr_2$	87·645
2AgBr to $SrBr_2$	87·653
2Ag to $SrCl_2$	87·642
2AgCl to $SrCl_2$	87·645
$SrBr_2$ to $SrSO_4$	87·629
$SrCl_2$ to $SrSO_4$	87·661
Mean of all	87·646

The value adopted by the authors is 87·65. Richards's figure is 87·62. An intermediate value, 87·63, is adopted in the new table.

Phosphorus.—Atomic weight re-determined by Baxter and Jones (*Journ. Am. Chem. Soc.*, xxxii., 298). From the ratio between silver and silver triphosphate the authors find P = 31 043, when Ag = 107·88. The rounded-off figure 31·04 is to be adopted.

Vanadium.—From the ratio between silver chloride and vanadyl trichloride, Prandtl and Bleyer find V = 50·963 and 51·133 in two series of experiments (*Zeit. Anorg. Chem.*, lxv., 152).

In a later paper, Prandtl and Bleyer (*Zeit. Anorg. Chem.*, lxvii., 257), also from analyses of vanadyl trichloride, find V = 51·061. From reductions of V_2O_5 to V_2O_3 they found V = 51·374. The latter method, however, they regard as uncertain. The value V = 51·06 may be provisionally adopted.

Tellurium.—Marckwald and Foizik (*Ber.*, xliii., 1710), by a somewhat complex volumetric process, based on the oxidation of TeO_2 by $KMnO_4$, conclude that Te = 127·61. (See also Browning and Flint, *Am. Journ. Sci.*, [4], xxviii., 347, who adduce evidence to show that tellurium is possibly complex). This agrees with many of the other recent determinations of the constant, but is not sufficiently exact to supplant the value given in the table.

Rhodium.—Two inaugural dissertations upon the atomic weight of rhodium have been issued from Gutbier's laboratory at Erlangen. Renz reduced rhodium pentammine bromide in hydrogen, and found Rh = 102·92. H. Dittmar (reproduced in *Sitz. Phys. Med. Soz. Erlangen*, xl., 184), by similar reductions of the corresponding chloride, found Rh = 102·93.

Platinum.—The very elaborate investigation of Archibald (*Proc. Roy. Soc. Edinburgh*, xxix., 721) upon the atomic weight of platinum was based upon analyses of the chloroplatinates and bromoplatinates of potassium and ammonium. In all, 28 ratios were measured, giving values for Pt ranging between 195·19 and 195·25. Their arithmetical mean gives Pt = 195·22. Archibald, however, in his final discussion, uses only 12 ratios, giving, in mean, Pt = 195·23. The figure 195·2 is given in the table.

The Inert Gases.—The densities and molecular weights of helium and neon have been re-determined by Watson (*Journ. Chem. Soc.*, xcvii., 810). For the atomic weights he finds He = 3·994 and Ne = 20·200. In another paper (*Journ. Chem. Soc.*, xcvii., 833) he applies the critical constants of krypton and xenon to their densities as determined by Moore, and finds Kr = 82·92 and Xe = 130·22. There are also new determinations of the density of argon, by Fischer and Hahnel (*Ber.*, xliii., 1435). Their mean value, referred to O = 16 is 19·945, a figure rather higher than that given by Ramsay and Travers. It corresponds to an atomic weight of A = 39·89.

It is also to be noted that a third revised edition of Clarke's "Re-calculation of the Atomic Weights" has recently been published by the Smithsonian Institution.

The annual table of atomic weights for 1911 is given with but few changes from that of the preceding year.

(Signed) F. W. CLARKE,
T. E. THORPE,
W. OSTWALD,
G. URBAIN.

ON THE ORIGIN OF COMETARY BODIES AND SATURN'S RINGS.*

By HENRY WILDE, D.Sc., D.C.L., F.R.S.

THE first part of this paper is a further exposition of the author's theory of the origin of comets and cometary bodies from the interior of the planets of the solar system, with new illustrations drawn from experimental mechanics, by which the direct and retrograde motions of cometary bodies are more fully explained. Dr. Wilde considers that the recently discovered satellites of Jupiter and Saturn which have retrograde motions are planetary ejectamenta, and from their comparative minuteness are hardly entitled to rank as satellites. The theory advanced by Olbers, the illustrious discoverer of Pallas and Vesta, that the planetoids are fragments of an exploded planet, finds confirmation in the great irregularities of their orbits, and the direct and retrograde motions of cometary bodies.

The author next discussed the origin of Saturn's rings, which has for a long time engaged the attention of natural philosophers. Kant assumed that Saturn at an early period of its history had the characteristics of a comet and that its tails contracted upon the planet and formed a ring. Laplace supposed the rings to be the original nebular substance uncondensed into the form of a satellite. The author ventures to affirm that the rings are the ejectamenta of Saturn when its diminishing energies were insufficient to eject a comet with its train of meteorites, or a cometary satellite. Dr. Wilde adduced evidence to show that the interior rings were formed some time subsequently to the outermost one, which is separated from the others by an annular space of 2585 miles. The author has drawn up a table of distances of the rings from Saturn, and the times of their revolutions calculated from his measurements of the fine photographs recently taken at the Lick Observatory. These elements surpass in accuracy those previously derived from observations and micrometric measurements.

Dr. Wilde reviewed the opinions of Kant on the origin of the Zodiacal Light, who considered it to be an efflux from the surface of the sun. Herschel and others have since regarded it as an accretion of cometary matter from outer space. Dr. Wilde considers that this singular object is an ejection from the interior of the sun of light elementary substances in a state of extreme subdivision and extending some distance beyond the earth's orbit.

CONVERSION FROM THE FERROUS TO THE FERRIC STATE.

By E. RATTENBURY HODGES.

A SIMPLE and striking illustration of this, such as the following, may not be generally known to teachers and lecturers.

If to a weak solution of ferrous chloride we add potassium sulphocyanate, a pink coloration appears, but on the addition of a drop or two of hydrogen peroxide, the conversion of the iron salt to the ferric condition is at once demonstrated by the formation of the familiar blood-red ferric sulphocyanate.

* Abstract of a Paper read before the Manchester Literary and Philosophical Society, October 4, 1910.

RESEARCHES UPON THE COMPLEXITY OF TELLURIUM.*

By WILLIAM R. FLINT.

(Concluded from p. 195).

Part II.—*Preliminary.*

Experiments upon a Fractionation by Nitric Acid.

In the purification of some crude tellurium by three crystallisations from nitric acid, by the method of Norris, Fay, and Edgerly (*Am. Chem. Journ.*, xxiii., 105), it was observed that a part was rather more insoluble than the rest, in the nitric acid used (sp. gr. 1·25). A separation was effected by decantation of the liquid from the less soluble portion. Both fractions were then evaporated to dryness and ignited to dioxide. Carefully weighed equal quantities of these samples were dissolved with equal amounts of hydrochloric acid, and diluted with equal amounts of boiling water. After standing for some hours, the precipitates were collected upon Gooch crucibles, and washed, dried, and weighed. It was found that the fraction more insoluble in nitric acid gave about 6·5 per cent more dioxide, by the hydrolysis from hot water, than the other, or more soluble, portion. It was proved that this difference was not due to the presence of impurities detectable by careful qualitative analysis.

A similar difference in solubility (in nitric acid) was noted in a re-crystallisation of part of the basic nitrate prepared from the 150-grm. portion of purified tellurium described in Part I. of this paper. After the whole of the sample taken had been finally gotten into solution, the greater part was thrown out, as basic nitrate, by sufficient concentration. and the liquid from which it had separated decanted from the crystals. These crystals were washed and dried in the heater as usual. The mother-liquor was then evaporated to dryness, and the residue ignited almost to redness, whereupon it developed an orange-red colour, and became distinctly crystalline in texture. The colour was proved not to be due either to iron or to selenium, by the ordinary tests.

Basic nitrate experiments performed upon the less soluble fraction, exactly as described in Part I., furnished the data (corrected) of the accompaning Table V.

Table V.

Exp.	$2TeO_2.HNO_3$ taken. Grms.	$2TeO_2$ found. Grms.		Atomic weight. of tellurium.
1.	1·98132	1·65281		126·53
2.	1·34204	1·11947		126·48
3.	1·36589	1·13945		126·55
4.	1·17057	0·97655		126·59
5.	1·07610	0·89765		126·50
6.	0·98468	0·82145		126·57
7.	1·67119	1·39396		126·44
8.	1·53443	1·28006		126·56
9.	2·53215	2·11231		126·53
10.	2·46437	2·05543		125·37
	16·12274	13·44914	Mean	126·51

The mean value found in this table, 126·5, is identical with that given by Browning and Flint as referred to in Part I. It is likewise practically identical with the mean, 126·58, of Table II. in the previous part. Whether this fact indicates that a more rapid fractionation can be secured by the hydrolysis of the nitrate than by that of the chloride, remains for further investigation to prove.

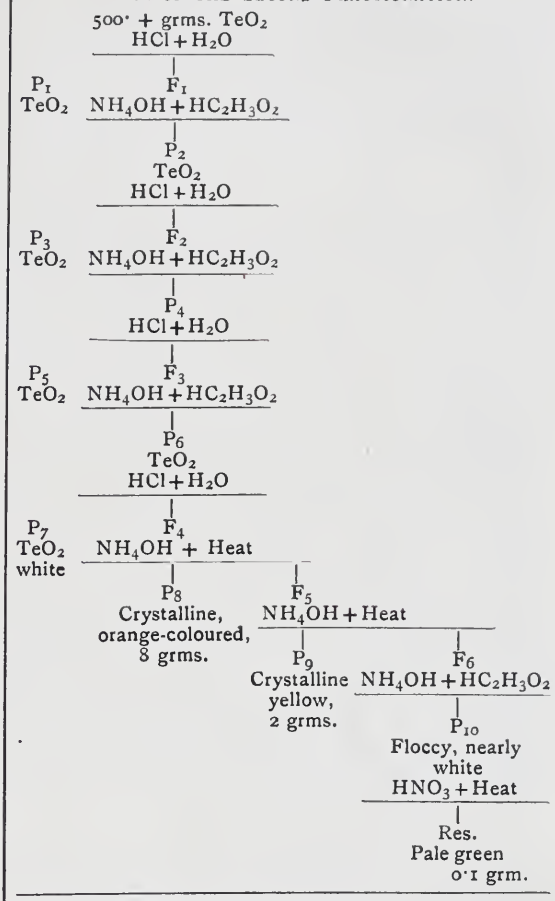
Atomic weight determinations of the more soluble fraction have not as yet been made.

Investigation of the Fraction less easily Hydrolysed by Water.

(See accompanying plan).

The tellurium in the filtrates from the water hydrolysis described in the preceding part was recovered by treatment with ammonia and acetic acid. The dioxide thus secured was next dissolved in hydrochloric acid, and the solution was diluted abundantly with boiling water and allowed to cool. The filtrate from the dioxide thus precipitated was again heated to boiling, and ammonia and acetic acid were added, in the usual way, to complete precipitation as dioxide of the remaining tellurium. This latter portion was re-treated in the same manner, and the process repeated twice more, each time using only the ammonia acetic acid precipitate from the preceding operation.

Plan of the Second Fractionation.



As the result of these four fractionations, almost exactly 500 grms. of dioxide were obtained by the water precipitation, while the unhydrolysed fraction secured by ammonia and acetic acid consisted of scarcely more than 10 grms. From the fifth repetition on the 10-grm. portion, a very small quantity of crystalline pure white dioxide was obtained by dilution and cooling of the hydrochloric acid solution. The filtrate was heated to boiling, and sufficient ammonia added to neutralise part of the acid, whereupon an orange coloured crystalline deposit, similar to that obtained in the nitric acid fractionation above described, began to form. Boiling for ten or fifteen minutes threw out about 8 grms. of this product, which was separated by decantation of the liquid, washed, and dried.

After filtering the liquid and re-heating it to boiling, more ammonia was added, but still not enough to neutralise all the acid present. By this means another crystalline deposit was secured, yellow in colour, and only a grm. or so in quantity. When the filtrate from the last mentioned substance was again heated, and finally precipitated completely by ammonia and acetic acid, a minute amount of floccy precipitate appeared. Nothing precipitable by

* From the *American Journal of Science*, xxx., p. 209.

stannous chloride in either acid or alkaline solution was found in the last filtrate, and it was therefore rejected. The floccy precipitate was collected on a filter, washed, and dried. Its amount was too small to admit of its being removed from the paper in any other way, and it was consequently dissolved off by nitric acid (sp. gr. 1·25), the solution filtered twice on asbestos, and evaporated to dryness. The final product, which was ignited nearly to redness, consisted of about one-tenth of a grm. of a pale green powder.

The colour of two of these substances suggested possible contamination by iron; that of the third by copper, or perhaps tungsten. No slightest traces of either iron or copper can be discovered by the usual tests. In hydrochloric acid solution all three give, with stannous chloride, black precipitates, similar to tellurium. No bismuth or antimony can be detected. In fact, all reactions so far tried appear to be identical with those given by tellurium, with one exception. When an excess of ammonia is added to a solution of the green substance in hydrochloric acid, the precipitate obtained by neutralisation of the acid is not completely dissolved by the excess of the alkali. The liquid filtered from this throws out a black substance, apparently tellurium, when acidified and treated with stannous chloride. The precipitate which did not dissolve in the excess of ammonia, when dissolved, after thorough washing, in hydrochloric acid, gives also a black precipitate with the same reagent. Since tungstic oxide is soluble in ammonia, but is not precipitated (although reduced to lower oxides) by stannous chloride, the presence of tungsten is apparently disproved. It is besides difficult to understand how an element having a fusing-point above 3000° C. could be volatilised with the tellurium in the process of distillation at a very much lower temperature than this.

By the use of a greater quantity of material, the investigator proposes to extract sufficient amounts of these products to enable him to determine their nature. This work is already begun, and a report upon it will be made as soon as it can be completed.

THE PART PLAYED BY MICRO-ORGANISMS OTHER THAN BACTERIA IN DETERMINING SOIL FERTILITY.*

By EDWARD JOHN RUSSELL, D.Sc.,
and
HENRY BROUGHAM HUTCHINSON, Ph D.

Of the various food-stuffs supplied by the soil to the plant the nitrogenous compounds, ammonia and nitrates, are among the most important; other things being equal the greater their amount in the soil the greater is the amount of plant growth. These compounds are not part of the original mineral constituents of the soil, but are formed by bacterial action from the organic matter invariably present—organic matter that has arisen from previous generations of plants, from bodies of animals, or from organic manures that have been added. The soil bacteria are thus producers of plant food; the more actively they work, the more fertile is the soil, while anything that limits their activity also limits the fertility of the soil.

It thus becomes of interest to examine the action of antiseptics on the soil. An antiseptic might be expected to stop the changes going on, and it actually does so while it remains in the soil. As soon as it is removed, however, the surviving spores germinate and give rise to a new crop of organisms. But a remarkable phenomenon is now observed: the new flora becomes far more numerous, and effects a much greater amount of decomposition than ever the old one did. Thus, when a soil was treated with toluene the number of organisms active and as spores was reduced from 6·7 to 2·6 millions per grm.; but when the soil was spread out for a few days so that the toluene could evaporate, then moistened and left, the number of organisms rapidly rose to 40 millions, and there was a corresponding increase in the amount of decomposition effected. Heating for two hours to 98°—a temperature insufficient to kill spores—led to the same result. The results of one experiment are given in Table I.

Pot experiments showed that the productiveness of the soil is notably increased by either method of treatment.

The first explanation suggested of these phenomena was that the spores had somehow been stimulated by the partial sterilisation, so that the new organisms were more virulent and efficient. This, however, was found not to be the case. Pure cultures of particular organisms—*B. mycoides*, a *Streptothrix*, and others—obtained from a toluened soil turned out to be less virulent than from the original untreated soil. Additions of small quantities of toluened soil to untreated soil did not lead to any great increase in bacterial activity, as it should if more virulent races were being introduced. On the contrary, the evidence all shows that the organisms are actually weakened by partial sterilisation; when the original organisms are re-introduced by means of small inoculations of untreated soil into toluened soil there is a marked increase in the number of bacteria and in the work they do, as shown in the second column of figures in Table II.

This observation, indeed, puts out of court all purely bacteriological explanations, as it shows that the original flora as such is more efficient than the new flora. Other experiments led to the same conclusion. We can neither assume a stimulated flora nor a flora made more effective through a change of type: we can only suppose that the new organisms effect more decomposition by reason of their greater number.

The problem is thus narrowed down to finding out what factor in the untreated soil is keeping down the bacterial population so that it does not rise above 10 or 16 millions, while in the toluened soil it runs up to 40 millions or more. The experiments already mentioned sufficiently prove that the factor is not bacterial. Nor is it a soluble toxin decomposed by toluene or chloroform; addition of an aqueous extract of the untreated soil to the toluened soil led to no depression, but, on the contrary, to an increase in the bacterial activity, due, as we found, to the introduction of some of the unweakened bacteria. Other chemical hypotheses also fell to the ground when we found that the injurious factor is capable of growth. Thus, in the experiments summarised in Table II. the addition of untreated to toluened soil leads at first to an increase in the number of bacteria. After forty days, however, the numbers begin to fall, and with greater rapidity as the proportion of untreated soil is increased; where 5 per cent was added the numbers fall from 60 to 26 millions, whilst when 20 per cent was added they drop from 45 to 6 millions.

We are therefore compelled to suppose that the factor is biological. Our results can be explained only on the assumption that there exists in ordinary untreated soil organisms keeping the bacteria in check. The organisms are not bacteria, and differ from them in at least three ways:—(1) They are not washed out from the soil to any extent, since the aqueous extract of the soil shows no deleterious effects; (2) they increase less rapidly than bacteria, as shown by the length of time that elapses before the inhibiting effect sets in (Table II.); (3) they are larger and less numerous than bacteria, since the small inoculation of untreated soil—0·5 per cent or less—does not invariably show the effect produced by a larger one. These are also the properties of protozoa, and we therefore looked for this class of organisms by adding soil to sterile hay infusion or to hay infusion-agar plates.

From the ordinary untreated soil some two dozen kinds of protozoa were obtained, including colpoda, amœbæ, monads, and others, which we found were capable of destroying bacteria in culture solution. From the toluened

* A Paper read before the British Association (Subsection B). Sheffield Meeting, 1910.

Table I.

	Number of bacteria per grm. of dry soil, in millions.			Ammonia and nitrate produced in nine days per million of dry soil.
	At beginning.	After nine days.	Increase during nine days.	
Untreated soil	6·7	9·8	3·1	0·7
Soil treated with toluene which was subsequently evaporated	2·6	40·6	38·0	17·1
Soil heated to 98°	0·0003	6·3 (*a*)	6·3 (*a*)	23·5

(*a*) After four days; nine days' count lost by plates liquefying.

Table II.

Soil treatment.	Number of bacteria per grm. of dry soil (millions)—			Ammonia and nitrates produced—	
	At start.	After 40 days.	After 100 days.	In 40 days.	In 100 days.
Untreated soil	11	16·0	3·5	1·3	7·0
Untreated + 5 per cent of toluened soil	11	23·3	7·0	6·4	10·0
Toluened soil	2	43·0	41·1	16·7	24·8
Toluened + 0·5 per cent untreated soil	2	59 6	28·2	15·7	32·8
Toluened + 5 per cent untreated soil	2	60·5	26·5	15·6	32·0
Toluened + 20 per cent untreated soil	4	45·1	6·0	16·4	27·5

soil no colpoda or amœbæ could be found, and only a few monads. Heated soil did not even contain monads.

Any process that kills these large organisms leads to an increase in bacterial numbers and activity and in soil productiveness. Heating to a temperature of 50° C. for an hour is effective, whilst 40° C. is not. Drying for ten days at 40° C. is effective, but for twenty-four hours is not. So with regard to antiseptics: ether, benzene, carbon disulphide, and petrol all act, but sodium sulphite and others do not. Exposure for some days in a vacuum is also effective. In all the experiments so far tried the parallelism is complete; where hay infusion cultures show that the protozoa are killed bacterial counts show that the numbers of bacteria have gone up, chemical analysis shows that the ammonia and nitrates have increased, and pot experiments show that the productiveness of the soil has gone up. Where, on the other hand, the protozoa have not been killed there has been no notable increase in any of these directions.

Again; conditions known to favour protozoa—the presence of much moisture and soluble organic matter—have a marked detrimental effect on the bacterial flora. The "wearing-out" of greenhouse soils and the deterioration of soils on sewage-treated farms are cases in point; investigations now in progress show that marked improvement sets in when such soils are heated or treated with toluene.

The indirect evidence that protozoa in the soil injuriously affect the bacteria is thus fairly complete, but direct evidence has not yet been satisfactorily obtained. The experimental difficulties of studying so opaque a substance as soil under the microscope and watching the movements of the micro-organisms have not yet been surmounted. Nor has it proved possible to grow the protozoa from a hay infusion culture in a toluened soil. These manipulative difficulties may in time be overcome; in the meantime we have only the indirect evidence.

It may be of interest to summarise the properties which the offending organism seems to possess. (1) It is larger than bacteria; (2) it grows only slowly compared with bacteria; (3) it is not readily detached from the soil by shaking with water, it may, indeed, very well be a protoplasmic film round the soil particles; (4) it is killed at 48° C. or thereabouts, and also by prolonged drying; (5) it may possibly arise from monads.

From the practical point of view experiments are in hand to discover some cheap and effective method of treating soils so that the injurious factor can be removed. Numerous pot experiments have demonstrated the possibility of obtaining crop increases varying from 20 to 100 per cent by treatment of the soil with a little toluene or by heat, but a number of mechanical and other difficulties have to be overcome before such methods could be applied to field practice.

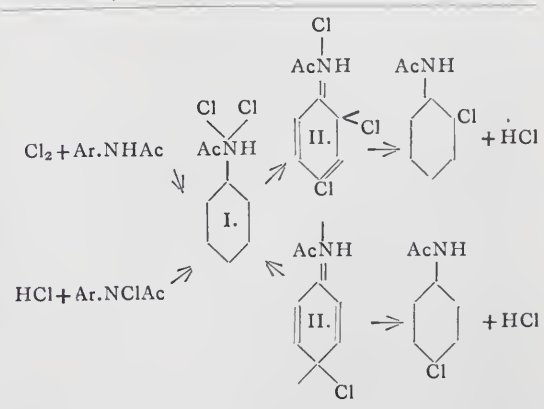
THE TRANSFORMATION OF NITROAMINES AND ALLIED SUBSTANCES, AND ITS RELATION TO SUBSTITUTION IN BENZENE DERIVATIVES.*

I. *The Chlorination of Anilides and the Transformation of Acychloroaminobenzenes.*

(*With* W. J. Jones, B.Sc.)

In summarising his views on substitution in aromatic compounds, Armstrong (*Reports*, 1899) expressed the belief that in the formation of derivatives of anilines and phenols, the reagent united directly with the nitrogen or oxygen, the residual valency of these atoms coming into play. In the case of anilines and anilides the definite compounds, which can often be isolated, nitroamines, chloroamines, &c., were held by Armstrong to be "a necessary stage in the formation" of the substituted aniline or anilide, the process of conversion being "regarded as one of isomeric change." He suggested further that, as part of the mechanism of the change, "the centric benzene nucleus assumed momentarily the highly unstable ethenoid form."

Later, Armstrong (*Trans. Chem. Soc.*, 1900, lxxvii., 1051) discovered that the chloroaminobenzenes were only converted into the isomeric chloroanilides in the presence of hydrochloric acid. Blanksma (*Receuil des Trav. Chim.*, 1903, xxii., 290) showed that under the conditions under which he worked the reaction was of the first order, and the speed proportional to the square of the concentration of the hydrogen chloride. It had been suggested by



* Report of the Committee, consisting of Prof. F. S. Kipping (Chairman), Prof. K. J. P. Orton (Secretary), Dr. S. Ruhemann, Dr. A. Lapworth, and Dr. J. T. Hewitt. Read before the British Association (Section B), Sheffield Meeting, 1910.

Orton (*Proc. Roy. Soc.*, 1902. lxxi., 156) that all such isomeric changes of the N-substituted derivatives under the influence of an acid catalyst were due to the formation of a complex or salt (I.) in which the nitrogen was quinquivalent. This compound was capable of undergoing an intra-molecular re-arrangement, in which the benzene nucleus shared, assuming an *o*- or *p*-quinonoid form (II.). The substituting group wandered in this re-arrangement into the *o*- or *p*-position, Thus the rigid adherence of anilines and anilides to the ortho-para law was accounted for.

Subsequently, Acree (*Am. Chem. Journ.*, 1907, xxxviii., 258) adopted the formation of the complex as the cause of the arrangement of chloroamines, and showed how, on this assumption, the speed of the change is proportional to the square of the concentration of hydrochloric acid, for the concentration of the reactive complex is proportional to the square of the concentration of the hydrogen chloride if it be ionised, thus :—

$$Ar.NHAcCl_2 \rightleftarrows Ar.NClAc + H + Cl'.$$

The discovery by Orton and Jones (*Trans. Chem. Soc.*, 1909, xcv., 14) that an equilibrium existed between chloroamine, hydrogen chloride, anilide, and chlorine, thus :— $K = [\text{chloroamine}][HCl]/[\text{anilide}][Cl_2]$; or, when the medium is 65 per cent acetic acid, or more dilute —

$$K^1 = [\text{chloramine}][HCl]^2/[\text{anilide}][Cl_2],$$

showed that other factors had to be taken into account. This equilibrium may be represented thus :—

$$Ar.NHAc + Cl_2 \rightleftarrows \text{complex} \rightleftarrows Ar.NClAc + HCl,$$

a relation which has been stated by Acree as a possibility. The facts of the case, however, do not appear to require in any way the existence of such an intermediary.

The discovery of the formation of free chlorine and anilide when hydrogen chloride reacts with chloroamine has led us to a new investigation of the transformation of chloroamines, and of the process of halogenation of anilides.

The Catalyst.—A great difficulty in the way of the "complex hypothesis" is the fact that hydrochloric acid alone has the power of bringing about the isomeric change of the chloroamine. Acree believed that other acids, and even chlorine and bromine, were similarly, but less powerfully, effective. But although we have examined this point very closely we have not been able to confirm his view.

In dilute acetic acid the change of the chloroamine occurs at first slowly, but gathering speed. Hydrogen chloride can always be detected. Thus, in 65 per cent acetic acid after half the chloroamine (initial concentration 0·025 grm.-molecule per litre) has disappeared one-sixteenth of the chlorine initially present in the chloroamine is found as hydrogen chloride.

The addition of sulphuric acid (nitric, perchloric, or hydrofluoric acid) somewhat increases the rate of change, some 10 per cent of the chlorine appearing as hydrogen chloride during the first half of the reaction.

The action of halogens was tested in carbon tetrachloride solution. (Obviously petroleum, which was used by Acree, is unsuitable for such experiments). With acetanilide, chlorine reacts instantaneously in this solvent, the insoluble *p*-chloro-derivative separating immediately. With the chloroamine there is no immediate reaction, then after an interval extending occasionally to days, a change begins, which finally attains considerable speed (Diagram exhibited); crystals of *p*-chloroacetanilide appear as soon as saturation for this substance is reached. If the quantity of chlorine suffices, further chlorination of this compound, and still more of the soluble *o*-chloro-derivative which is produced simultaneously, follows.

In both reactions the halogen attacks either a minute quantity of anilide present with the chloroamine, or more probably a trace of some impurity, yielding hydrogen chloride or bromide, which then reacts with the chloroamine. In carbon tetrachloride it has been shown (by the aspiration-method) in the case of anilides which do not chlorinate, that the reaction,—

$$Ar.NClAc + HCl = Ar.NHAc + Cl^2,$$

is quantitative.

In the base of bromine the reactions are (after the formation of a trace of hydrogen bromide) : —

$Ar.NClAc + HBr = Ar.NHAc + BrCl = BrAr.NHAc + HCl$;

$Ar.NClAc + HCl = Ar.NHAc + Cl_2$; $Cl_2 + Br_2 = 2BrCl$.

Bromine chloride has been shown to be stable in carbon tetrachloride and other anhydrous solutions, and to be a most powerful brominating agent of anilides. The reactions proceed until the bromide is exhausted, when chlorination begins.

These experiments show further that chloroamines cannot be directly chlorinated or brominated.

Comparison of the Direct Action of Chlorine on Anilides with the Conversion of Chloroamines in the presence of Hydrochloric Acid.

1. In glacial acetic acid the two processes, chlorine on anilide and hydrochloric acid on chloroamine, give an identical rate of chlorination. It is a reaction of the second order, for acetanilide $k_{II} = 40$, and for *p*-chloroacetanilide $k_{II} = 0{\cdot}21$. In glacial acetic acid the equilibrium,—

$$Ar.NHAc + Cl_2 \rightleftarrows Ar.NClAc + HCl,$$

gives an inappreciable amount of chloroamine and hydrochloric acid.

The effect of small quantities of water is to accelerate the chlorination in a direct ratio. But after the addition of 4 to 5 per cent the water begins to affect the equilibrium and favours the production of chloroamine and hydrochloric acid.

The speed of chlorination when the system is made up of chloroamine and hydrochloric acid still continues to increase, but as the Curve I. shows, only to a composition of the medium 92 per cent acetic acid, when the speed begins to decrease. Curves II. and III. show respectively the falling off in two systems in the amount of chlorine and anilide with dilution of the acetic acid.

2. In dilute acetic acids the rate of formation of C-chloro-derivatives is very different in the two cases. On bringing together aniline and chlorine a very rapid formation of both C-chloro- and N-chloro-derivative occurs, a very small proportion of the chlorine (measured by aspiration) remaining free in the system. The relative proportions of the two compounds, which vary with the anilide and the composition of the medium, is shown in the table.

TABLE I.—*Ratio of* $\frac{\text{Chloroamine}}{\text{Chloroanilide}}$ *from Interaction of Chlorine and Anilide.* $T = 15°$.

Medium. Percentage acetic acid (by volume).	Acetanilide.	*p*-Chloroacetanilide.
0	0·07/1	—
30	0·082/1	0·93/1
50	0·08/1	1·25/1
65	0·083/1	1·55/1

TABLE II.

Medium. Dilute acetic acid.	Acetylchloroaminobenzene (conc. 0·025). Conc. HCl.	k_1.	n.	Acetyl-*p*-chloroaminobenzene (conc. 0·025). Conc. HCl.	k_1.	n.
50 per cent	0·025	0·00039	1·94	0·025	0·00053	1·36
	0·05	0·0015		0·050	0·00135	1·33
65 ,,	0·025	0·0026	1·60	0·025	0·0023	1·43
	0·05	0·0078		0·05	0·0062	
75 ,,	0·025	0·0126	1·70	0·075	0·0093	1·27
	0·05	0·43				

The N-chloro-derivative slowly disappears, and is replaced by the chlorinated anilide.

The conversion of the chloroamine in the presence of hydrochloric acid, on the other hand, is a slow, regular, apparently monomolecular reaction, the speed of which is,

in dilute (below 50 per cent) acetic acid, proportional to the square of the concentration of the hydrochloric acid. Table II. shows, however, that this relation only holds within narrow limits.

Under "n" is given the values from the equation—

$$\frac{k}{k'_1} = \frac{HCl^n}{HCl'^n};$$

whence—

$$n = \log \frac{k}{k'_1} \Big/ \log \frac{HCl}{HCl'}.$$

Further, the apparently monomolecular character of the reaction is not maintained throughout the change. The product, the chlorinated anilide, even when incapable of further chlorination, exerts a disturbing influence causing a decrease of the rate. This is well shown in the case of *p*-chloroacetylchloroaminobenzene, which yields 2 : 4-dichloroacetanilide.

TABLE III.

Time (in minutes).	Percentage of chloroamine converted.	k_1
	Experiment A.	
128	26·2	0·0027
213	39·1	0·0023
300	48·5	0·0017
407	57·2	0·0017
590	67·4	0·0015
758	73·2	0·0012
954	78·2	0·001
	Experiment B.	
18	1·72	0·0007
100	7·8	0·0007
301	21·2	0·00076
428	32·1	0·00078
687	41·1	0·00076
826	45·4	0·00072
1096	54·8	0·00072

Experiment A. - *p* - Chloroacetylchloroaminobenzene = 0·025 grm. mol. per litre. HCl = 0·025 grm. mol. Medium, 65 per cent acetic acid.

Experiment B.—As in Experiment A, but in addition 1 gr. mol. proportion of 2 : 4-dichloroacetanilide.

In order to understand more fully the influence of the anilide which is produced on the conversion of the chloroamine, the effect of the presence of a second anilide on the equilibrium between chlorine and anilide must be considered.

Equilibrium between Chlorine and Anilide in Systems containing more than one Anilide.

If 1 grm. molecular proportion of an anilide B is added to a system prepared from 1 molecular proportion of chloroamine of anilide A, and 1 molecular proportion of hydrochloric acid, a rapid re-adjustment occurs to a final equilibrium which is in accord with the two equations :—

$$[\text{Chloroamine A}]\,[HCl]^2/[\text{Anilide A}]\,[Cl_2] = K_A.$$
$$[\text{Chloroamine B}]\,[HCl]^2/[\text{Anilide B}]\,[Cl_2] = K_B.$$

Since $[Cl_2]$ and $[HCl]^2$ are identical in the two equations, we have :—

$$\frac{\text{Chloroamine A}}{\text{Anilide A}} \Big/ \frac{\text{Chloroamine B}}{\text{Anilide B}} = K_A/K_B.$$

In 65 per cent acetic acid, the $[Cl_2]$ is generally negligible, and hence the relative amounts of each anilide and chloroamine can be easily calculated. When the $[Cl_2]$ has an appreciable value, the calculations of the composition of the system involves the solution of a quintic equation.

In 90 per cent acetic acid and above the equilibrium equation contains the first instead of the second power of the concentration of the hydrochloric acid, and the calculation of the composition is by means of a cubic equation which has been solved. Thus in a system made up from molecular proportions (0·025 grm. mol. per litre) of *s*-tribromoacetanilide, hydrochloric acid, and acetylchloroamino-*p*-nitrobenzene (or from *p*-nitroacetanilide, hydrochloric acid, and acetyl-chloroamino-*s*-tribromobenzene), 59 per cent of the chlorine originally as chloroamine was found to be free, whilst 60 per cent was the amount calculated. For comparison in the system prepared from *s*-tribromoacetanilide and chlorine, the free chlorine is 57 per cent, whilst in that prepared from *p*-nitroacetanilide and chlorine, the free chlorine is 89 per cent.

In the case of *p*-chloroacetanilide and 2 : 4-dichloroacetanilide quoted above, where the value of K (in 65 per cent acetic acid) for the former is 8·1 and for the latter 4·47, it is calculated that in the system when half the chloroamine has been converted into 2 : 4-dichloroacetanilide, the concentrates of the anilides and chloroamines are as follows :—

$$[p\text{-}Cl.C_6H_4.NClAc] = [2 : 4\text{-}Cl_2.C_6H_3.NHAc] = 0·0072,$$
$$[p\text{-}Cl.C_6H_4.NHAc] = [2 : 4\text{-}Cl_2.C_6H_3.NClAc] = 0·0053;$$

that is the concentration of the chloroamine, which in changing is 0·0072 instead of 0·025/2 = 0·0125.

Chlorination of an Anilide by the Chloroamine of another Anilide.—The chloroamine of such an anilide as 2 : 4-dichloroacetanilide is in the presence of hydrochloric acid a chlorinating agent for acetanilide. Thus in 65 per cent acetic acid rapid chlorination follows the addition of a grm. molecular proportion of acetanilide to grm. molecular proportions of the chloroamine and hydrochloric acid (where 6 per cent of the chlorine is free). The chlorination is far more speedy, $k_1 = 0·42$, than in the transformation of acetylchloroaminobenzene, $k_1 = 0·0026$.

In 50 per cent acetic acid, where a far smaller percentage of chlorine is free, $k = 0·00039$ for the transformation of the chloroamine, and 0·01 for the action of the chloroamine on the anilide.

(To be continued).

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,*

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, &c.

By PERCY H WALKER.

(Continued from p. 197).

Glycerin.

As a rule, no determinations are necessary on glycerin except ash and specific gravity.

1. *Ash.*—Ignite 10 grms. at a low temperature, either in the muffle or in a hood having a very good draft.

2. *Specific Gravity.*—Determine with a pyknometer at 15·5 C.

3. *Refractive Index.*—Determine with a Zeiss direct reading refractometer at 15° or 17·5° C. With a pure article the per cent of glycerin may be obtained from either the specific gravity or the refractive index (Lewkowitsch, "Oils, Fats, and Waxes," 1909, iii., 327).

4. *Chemical Method of Determining Glycerol.*—In impure glycerin, such as soap lye, a determination by physical methods is, of course, not reliable. For some mixtures, containing other reducing bodies, there is no really good method. When a chemical method is necessary, and sugar and other organic compounds are absent, Hehner's bichromate method is probably as satisfactory as any available. Place the crude glycerin (about 1·5 grm.), or a corresponding amount of soap lye, from which all fatty acids have been removed, in a graduated 100 cc. flask, dilute slightly, add some oxide of silver, allow to stand ten minutes, and add a slight excess of basic lead acetate. Make up to the mark, filter through a dry paper, and place 25 cc. of the filtrate in a perfectly clean beaker. Add first an accurately measured amount (40 to 50 cc.) of a solution of bichromate (made by dissolving 74·86 grms. of potassium bichromate in water and diluting to 1000 cc., the exact strength being then determined against pure iron or ferrous

* *Bulletin* No. 109, Revised, U.S. Department of Agriculture, Bureau of Chemistry.

ammonium sulphate), then 15 cc. of strong sulphuric acid. Cover the beaker and heat for two hours in boiling water; then cool. Add an excess of standard ferrous ammonium sulphate solution and titrate back with a standard bichromate solution containing 7·486 grms. per litre. (The ferrous ammonium sulphate solution should contain about 240 grms. per 1000 cc.). One cubic centimetre of the strong bichromate solution corresponds to 0·01 grm. of glycerol.

Inking Pads.

The material used in these pads is printers's roller composition, being composed of glue and glycerin generally with a small amount of borax added.

1. *Sampling.*—Weigh the whole pads, remove the felt and weigh again. Cut the pad in quarters, and when only one pad is furnished cut up two opposite quarters into very small and uniform pieces. When several pads are in one sample, take smaller segments from each pad. It is very important that the samples be all cut to a uniform size—cubes about 2 mm. on each edge.

2. *Moisture.*—Cover the bottom of a small flat-bottomed aluminium dish (2·5 inches in diameter, and five-eighths of an inch high) with freshly ignited sand, weigh, distribute over the sand from 1·5 to 2 grms. of the fine pieces of pad, weigh accurately, and heat for two hours in a water-oven, cool in a desiccator, and weigh. Duplicates should agree within 0·3 per cent.

3. *Ash.*—Char carefully 10 grms. of the sample in a 100 cc., or larger, platinum dish, extract with water, filter, burn filter and carbonaceous matter, add water extract, evaporate, and heat to low red-heat.

4. *Borax.*—To 30 grms. of the sample in a large platinum dish add 5 cc. of a 20 per cent solution of sodium hydroxide and 10 cc. of a saturated solution of barium hydroxide, char, extract with water and dilute hydrochloric acid, ash the residue, and extract the ash with dilute hydrochloric acid. Transfer to a 250 cc. graduated flask, add about 0·5 grm. of calcium chloride and a few drops of phenolphthalein, then a 10 per cent solution of sodium hydroxide until slightly alkaline, followed by 25 cc. of lime water. Make up to mark, mix, filter through a dry paper, and titrate 100 cc. with half-normal sulphuric acid until the pink colour disappears, then add methyl orange and continue the addition of half-normal sulphuric acid until the yellow is changed to pink. Add fifth-normal sodium hydroxide until the solution is exactly neutral to methyl orange; boil until all carbon dioxide is driven off, cool, add almost enough mannite to saturate the solution. Add phenolphthalein and titrate with fifth-normal sodium hydroxide. One cc. of fifth-normal sodium hydroxide corresponds to 0·0191 grm. $Na_2B_4O_7.10H_2O$; 0·0101 grm. $Na_2B_4O_7$; 0·0124 grm. H_3BO_3; 0·007 grm. B_2O_3.

5. *Gelatin.*—Determine the nitrogen and multiply by 5·56. From the moisture and gelatin, if these values are known for the glue originally used, an approximation of the amount of glue used in making the pad can be calculated. The ash is only a rough check, as some of the boric acid is lost on burning.

Lubricating Oils.

1. *Specific Gravity.*—Determine in the regular manner (see *ante*).

2. *Flash and Fire-points.*—Follow the method given under Linseed Oil (*ante*).

3. *Viscosity.*—Strain the oil through bolting cloth and determine the viscosity by the Engler-Ubbelohde method (Ubbelohde, "Handbuch der Oel und Fette," i., 341). Great care should be taken to have the apparatus thoroughly clean, and the temperature of the oil must not vary.

4. *Ash.*—Burn 10 grms. of the oil at as low a temperature as possible, using a quartz or porcelain dish. (Do not use platinum, as some lubricating oils contain lead soaps). Determine the reaction of the ash with litmus-paper. The amount of ash should be very small and neutral unless the oil contains soap, when the reaction will be alkaline, unless it is a lead soap.

5. *Reaction of Oil.*—Heat about 20 grms. of the oil with 50 cc. of water, draw off the water and test its reaction with litmus. If the reaction is acid it is probably due to sulphuric acid; test with barium chloride.

6. *Action on Copper.*—Spread some of the oil on a bright polished piece of copper and expose to the air for twenty-four hours. The copper should not corrode or turn green.

7. *Tarry and Suspended Matter.*—Place 5 cc. of the oil in a pear-shaped separatory funnel of about 200 cc. capacity, add 95 cc. of gasoline, shake well, and allow to stand fifteen minutes. No precipitate should appear.

8. *Cold Test.*—Warm the oil up to 80° C., and if it contains any solid particles keep at 80° until they are completely melted. Put 50 cc. of the oil in a dry 4-ounce bottle, provided with a stopper through which passes a thermometer. Place in a freezing mixture and stir gently with the thermometer until the oil is frozen, insert the cork, and leave the bottle in the freezing mixture for an hour. Then remove from the bath, wipe dry, and place in a beaker packed with dry asbestos to insulate the sides of the bottle. Break up and stir the oil with the thermometer; invert the bottle at every degree of rise in temperature, and note the temperature at which the oil will flow from one end of the bottle to the other in fifteen seconds. For the freezing mixture for temperatures above 2° C. use ice and water, for lower temperatures use ice and salt, or, if necessary, crystallised calcium chloride and snow or shaved ice.

9. *Volatility.*—Heat from 0·5 to 1·5 grm. of oil in a flat-bottomed dish in a bath at the temperature of boiling water for four hours.

10. *Fatty Oils (Qualitative Test).*—Heat 4 or 5 cc. of the oil in a test-tube with a piece of caustic soda (solid) for fifteen minutes at a temperature of 230° to 250° C. Allow to cool. The presence of fatty oil is indicated by the gelatinisation, complete or partial, of the contents of the tube.

11. *Quantitative Determination.*—In the presence of large quantities of mineral oil, saponification with alcoholic potash takes a long time, since the mineral oil prevents the potash coming in contact with the fatty oil. Schreiber's method (*Journ. Am. Chem. Soc.*, 1907, xxix., 74) gives good results in a short time. Weigh 5 grms. of the oil in a 200 cc. Erlenmeyer flask, add 25 to 50 cc. of half-normal alcoholic potash and sufficient benzol (C_6H_6) to dissolve the oil when warmed (generally 25 cc. is enough, but with heavy cylinder oils as much as 50 cc. may be necessary; in this case it is well to add 25 cc. of neutral alcohol). Connect the flask with a 3-foot condenser and set it on the iron plate that forms the top of the steam-bath, so that the steam will not strike it directly, and regulate the heat so that the condensing liquid will not be forced to the top of the condenser. In this way the contents of the flask can be boiled without apparently losing any of the solvent. Boil for thirty minutes. Cool, add phenolphthalein, and titrate the excess of potassium hydroxide with half-normal sulphuric acid. On adding the acid the liquid separates into two layers and the change in colour can be seen in the lower layer; the titrating, however, must be conducted slowly. Subtract the cubic centimetres of sulphuric acid from the amount used on blanks and calculate the saponification number. For all practical purposes 195 may be considered as the saponification number of the fatty oils used in lubricating oils, and hence if S equals the determined saponification number, 100 S divided by 195 equals the percentage of fatty oil present. When the oil is very dark, or when soaps are present, it may be necessary to determine the hydrocarbon oils directly. For this purpose saponify as described, cool, add 25 cc. of benzol, transfer to a separatory funnel, add 100 cc. of water, shake, allow to settle, draw off the water layer, and wash the benzol three times with 100 cc. of water; wash the soap solution with three portions of 50 cc. of benzol, evaporate off the benzol solution, and weigh the non-volatile hydrocarbon oils.

12. *Acid Number.*—See Linseed Oil (*ante*).

13. *Rosin Oil.*—See Linseed Oil (*ante*).

(To be continued).

APPARATUS FOR THE COMMERCIAL PRODUCTION OF OZONE.

THE valuable properties of ozone both as a chemical reagent and as a means of research have long been known, and have been brought recently into prominence in connection with the purification of water and air upon a large scale.

The "Ozonair" Company have placed upon the market a number of different forms of ozone generators adapted to meet all requirements, and more recently attention has been given to the perfection of sets of apparatus for laboratory and research work. The particular form of generator that the company manufacture gives a large yield of ozone free from the oxides of nitrogen; the mechanical details are carefully arranged, and the machines do not readily get out of order. Where alternating current is used suitable switchboards and transformers are supplied for providing the suitable high tension current to operate the generator, and for continuous current installations various forms of motor convertors are available. A great many plants have been designed and constructed by the Company for a variety of purposes. A new form of generator specially devised for research laboratories is shown in Fig. 1. It is so constructed that it will withstand great pressure, and with it experiments involving the use of ozonised air under pressure can be carried out; it contains a number of electrodes of special design in a cast-iron case which is

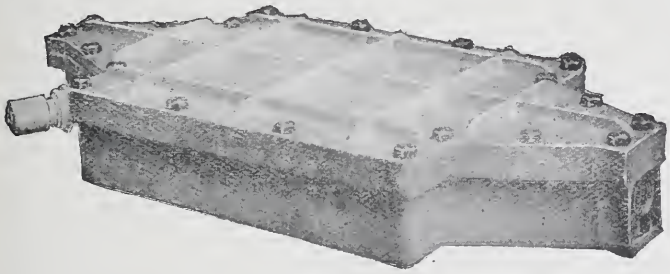


FIG. 1.

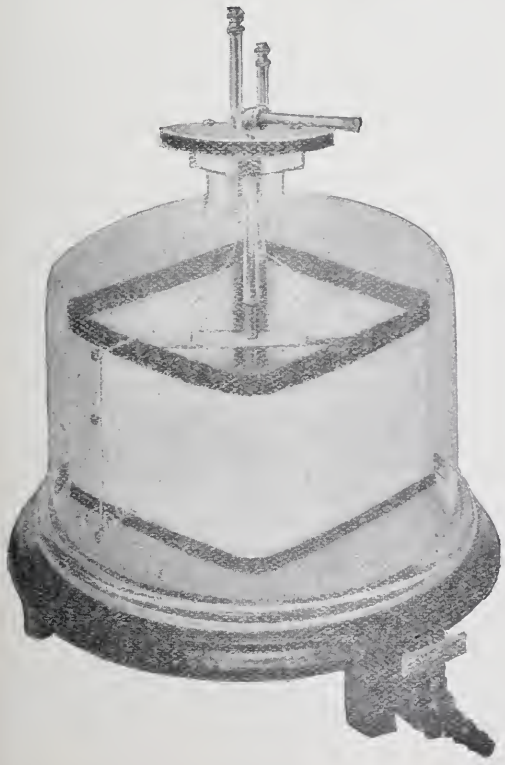


FIG. 2.

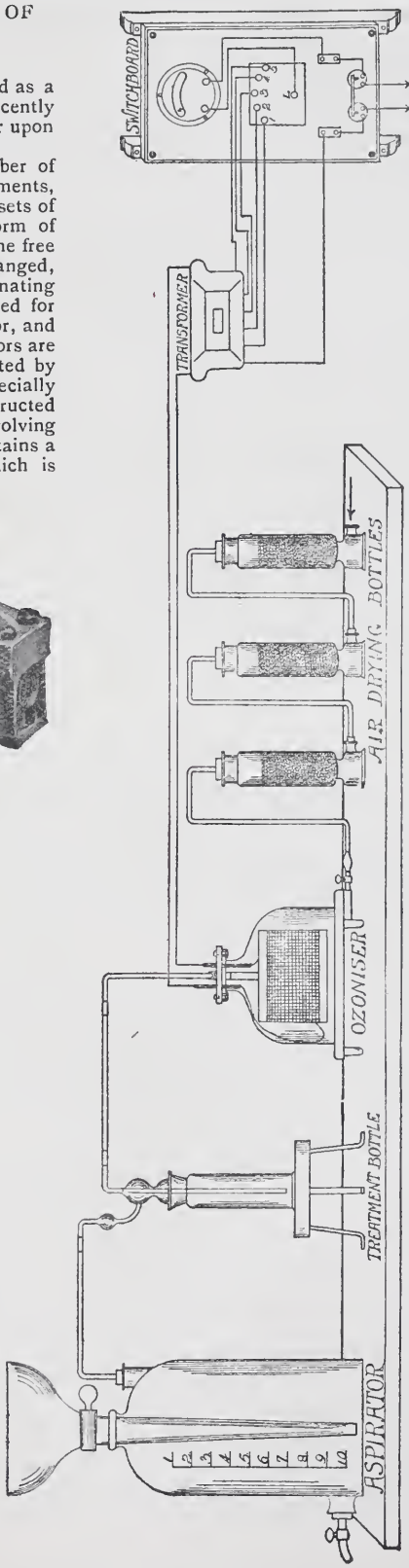


FIG. 3.

galvanised and water-tight; the high-tension connecting cables are arranged with plug fittings, so that if desired they can be readily disconnected.

With an energy consumption in the generator of 100 watts, the yield of ozone is about 4 grms. per hour at a concentration sufficient to sterilise water, bleach oils, &c. The capacity for bleaching in a day of ten hours is about 50 lbs. of material, and for sterilising water about 4000 gallons. Naturally at lower concentrations the yield will be greater, and *vice versa*.

A useful form of experimental apparatus for the lecture table is shown in Fig. 2. It consists of a small generator enclosed in a bell-glass and mounted upon a glass-faced iron tripod stand with a stopcock; the neck of the bell-glass is fitted with a cap and carries the high tension terminal and draw-off tube for the ozone.

In addition to generators aad electrical apparatus the Company supply complete sets of glass aspirators, drying-bottles, and experimental chambers for carrying out researches upon the effects of ozone; one of these plants is shown in Fig. 3. We have recently had occasion to use one of the Company's generators for some experiments upon the bactericidal action of ozone, where freedom from the oxide of nitrogen was essential, and we found the ozone pure and the method of generating it easy and trustworthy. In these special experiments over 90 per cent of the microbes were killed.

The Ozonair Company are prepared to give advice and to design plants for the production of ozone upon any scale and for any purpose that may be required, and at their laboratories a staff of experts can be consulted and experimental work carried out by arrangement.

THE SIR JOHN CASS TECHNICAL INSTITUTE.

The Inaugural Lecture of the courses of instruction in "Fuel" was given by Mr. J. S. S. Brame, Lecturer on Fuel, at the Institute, on Monday, October 10th. The subject of the lecture was "Power Gas and its Development." The Chair was taken by Prof. F. Clowes, D.Sc., Past-President of the Society of Chemical Industry, who, in introducing the lecturer, pointed out the technical importance of the modern developments of power gas, and referred to the value of the instruction that is provided at the Institute for the study of the applications and analytical examination of all forms of fuel.

Mr. Brame pointed out that the introduction in quite recent years of power gas, whereby the heat units available in our fuels are converted into work without the intermediary of the steam-engine, has been a factor of immense economical importance, and the extension of this method of applying our fuel will, in the near future, exercise an even greater influence in reducing the cost of power, and thus enabling us to conserve our vast, but nevertheless limited, supplies of coal.

The total coal production for 1909 was 263,758,000 tons, and our annual home consumption some 180,000,000 tons. It is difficult to estimate how this consumption is distributed, but we may roughly compute that 45 millions are utilised for power purposes, 20 millions for blast furnaces, whilst some 17 millions are carbonised for the production of gas. It is unlikely that the consumption in gas works will decrease, but the introduction of the large gas-engine is rendering much of the available power from blast-furnace and coke-oven gas—equivalent to some 1,250,000 horse-power per day—of service, thus leading to very considerable fuel economy; indeed one English firm is saving about £1000 per week on these lines, and on the Continent the Differgingen Iron and Steel Works effect a fuel saving of £75,000 in the year.

It is to the demand of coal for power purposes that we must turn to realise the economies which are possible through the introduction of power gas. As compared with the steam-engine the consumption of coal per B.H.P. is practically one-half, and if we could reduce our coal consumption by 9 million tons by substituting power gas, a national saving of 20 per cent on the coal used for power would be effected. Further, the power gas plant is rendering economically available for power purposes immense stores of fuel which could not otherwise be applied. One ton of dry peat, for example, yields some 1000 B.H.P. per hour, together with from 70 to 200 lbs. of sulphate of ammonia, worth £11 to £12 per ton. When it is remembered that in Europe there are some 140 million acres of peat bog, often 14 to 16 feet in thickness, the utilisation of a small portion of the energy here stored up would effect a large saving of coal for other purposes.

The possibilites of power gas are being rapidly recognised, as is evident by the enormous advances made in its introduction in large and small works in recent years. Where gas for heating purposes as well as power is demanded, it offers so many advantages that its installation into steel works, ship-building firms, and similar industries already amounts to many thousand horse-power.

As regards fuel costs, the efficiency of power gas is approximately 20 per cent, whilst with steam 9 to 10 per cent is a fair average.

An outline of the general principles underlying the action of gas plants was then given and the general arrangement of plant illustrated, the various forms of pressure plants and suction plants being described.

For small powers suction gas is not a competitor with pressure gas from bituminous fuels, since gas plants using this class of fuel are unsuited for small powers by reason of their higher first costs and working charges.

The pressure plants for non-bituminous fuels offer great advantages where gas is required for heating in addition to power. Pressure gas is usually somewhat richer than suction gas and is more uniform in composition, since its production is continuous whilst the latter is intermittent. Pressure systems usually are provided with a holder which enables more uniform gas to be stored, supplies good gas to the engine after a stand-by or working on light load, and eaables gas to be distributed to several engines and to furnaces for heating.

On the other hand, for small power plants only, up to some 250 horse-power, the suction gas plant offers so many advantages, such as compactness, low cost, simplicity of working, that its rapid introduction throughout all countries is easily understood. Hitherto the choice of fuels has been limited to anthracite (the demand for which has greatly raised the price) and good quality coke. The use of bituminous fuel, with its manifest advantages in the matter of supply and price, has until quite recently been impossible owing to the difficulty of removing the tar from the gas, but practically all the leading makers now supply suction plants which it is claimed work well with such fuels, the general principle involved being the destruction of the tar by causing the distillation products from the coal to be drawn through the hottest zone of the producers where the resulting coke is being gasified. In Germany suction plants working on fuels containing sufficient moisture for the producer reactions—lignite, peat, &c.—have been successfully employed.

In comparing the relative merits of coal-gas and suction gas for small power plants detailed estimates of cost were given, which showed that little advantage is obtained by the adoption of suction gas when cheap town gas is available, what little gain there is being quite counterbalanced by the convenience arising from town gas supply and total absence of stand-by charges. Above 30 horse-power the advantage of suction gas, however, rapidly increases.

The success of the suction plant working on bituminous fuels, even of the most unpromising character, is now established, and the extension of the use of this type of plant is likely to be very rapid. Systems of scrubbing the gas will be improved when it is realised that such a process is essentially not a filtering one. The utilisation of the exhaust from the engine in lieu of steam through the producer has given promising results, the poor quality of gas

being more than counterbalanced by the higher compressions possible in the cylinder. The abolition of the gas-holder where pressure gas is required for power purposes only, and the control of production according to demand by fans automatically working with the engine, is almost universal in German practice.

The course of lectures on "Liquid, Gaseous, and Solid Fuel," by Mr. Brame, commenced on Monday, October 17th. The full syllabus of the course may be had upon application to the Principal, The Sir John Cass Technical Institute, Jewry Street, Aldgate, E.C.

The Inaugural Lecture of the course of instruction in the "Fermentation Industries" was given by Mr. S. O. Nevile, of Messrs. Brandon's Putney Brewery, Ltd., on Tuesday, October 11th, the subject of the lecture being "The Economic Use of Coal in the Brewing Industry."

Mr. Nevile pointed out that the economic value of a coal depends upon the relationship between its efficiency and its price, the efficiency of the different kinds varying with every condition of combustion, and the price with the location of the consumer, owing to the large proportion of the cost being represented by the expense of freight.

A general idea of the efficiency of the coal may be obtained from the analysis and general description, but having selected a coal which appears to suit the requirements of the consumer, as regards quality and price, a practical test under the conditions obtaining in the brewery is the only sure proof of its efficiency.

Generally the most convenient form of power is found to be the steam-engine, owing to its great elasticity of power, and for brewery purposes it may be considered to be as economical as any.

For ordinary factory purposes the gas-engine, working with producer gas, is doubtless the most economical, but a brewery differs from an ordinary factory inasmuch as there can be found a profitable use for the exhaust steam discharged from the engine, and inasmuch as it does not appear easy to make much practical use of the waste gases discharged from the gas-engine, the steam-engine will be found to be the more economical of the two if it be credited with the heat contained in the exhaust steam for which a profitable use can be found.

Steam is not only required for producing power, but is also used for heating water both for the brewing of the beer and for cleansing purposes, and sometimes for cooking the beer; consequently when discussing the question of fuel the economy of the steam-boiler is the most important consideration.

If a supply of cheap low grade fuel is obtainable, such as small coal or coke breeze, a satisfactory economy may be effected by installing a special furnace to use whatever form of cheap fuel is available.

Having selected the fuel, the first consideration is to ascertain that the combustion is satisfactory, and since the proportion of carbon dioxide in the flue gases is an index of satisfactory combustion, one of the instruments recording the amount of CO_2 contained in the gases will be an advantage.

After having effected a satisfactory combustion it is necessary to see that the flue gases are not allowed to escape at too high a temperature; should this be found to be above 500° F. an economiser, which will heat the feed water on the way to the boiler, can be installed to advantage. The exhaust steam discharged from the engine furnishes an opportunity of saving fuel, as under ordinary circumstances this exhaust steam is sufficient to heat up the whole of the water required for cleansing purposes.

Another satisfactory economy may be found in utilising the heat given up by the worts when cooling, and if the brewing water be used through the refrigerator a convenient method of effecting this economy is to allow this to run direct to the brewing backs for the next day's brewing. A further economy can be found by using the steam evaporated from the beer while boiling, and if the necessary apparatus be installed this may be utilised by raising the water already partially heated by the refrigerator to the necessary brewing temperature.

It appears to be practicable to brew beer with as small a consumption as 20 lbs. of coal per barrel of beer brewed, but it is highly improbable that all the conditions which favour this extreme economy can be assembled in one particular brewery.

In approaching this question of economy of fuel it must never be forgotten that the flavour and the quality of the beer brewed must always be considered to be the principal consideration. Consequently, whilst one is on safe ground in increasing the efficiency of one's steam-raising plant, and utilising the exhaust steam from the steam-engine, the question of economising the fuel used for cooking the beer must be approached with the utmost caution.

The course of lectures on "Brewing and Malting" commenced on Tuesday, October 18th. The full syllabus of the course may be had upon application to the Principal, The Sir John Cass Technical Institute, Jewry Street, Aldgate, E.C.

NOTICES OF BOOKS.

Thirty-fourth Annual Report of His Majesty's Inspectors of Explosives. London: Wyman and Sons, Ltd. 1910.

The Thirty-fourth Annual Report contains the usual tabulated statements of accidents due to explosives which occurred during the year 1909 as well as the general tables showing the inspections and searches undertaken by the inspectors. The report of the chemical advisers contains an exhaustive list of the explosives which have been subjected to heat and composition tests, including many new substances, but the chemists' time having been fully occupied with their work for the Heat Test Committee they have no accounts of special work to present.

A First Year's Course of Inorganic Chemistry. By G. F. Hood, M.A. (Oxon.), B.Sc. (Lond.). London: Rivingtons. 1910.

This little book contains a full year's course of elementary practical chemistry. The order is very much the same as that now generally adopted, and there are no startling novelties of treatment. The various experiments to be performed are discussed in simple and clear language, the explanations are to the point, and generally speaking the definitions are good. Suggestions are given for various exercises to be carried out by the class in addition to the course of sixty-five experiments, and these are generally well chosen and instructive. In places, however, it would seem that rather fuller details of the experimental arrangement would be an advantage, and possibly hardly enough warnings and precautions are given for beginners who are dealing with unknown and sometimes dangerous substances. Strict supervision of all the work done in the laboratory would do away with the necessity of emphasising the need of caution, but experience shows that printed warnings never come amiss.

CORRESPONDENCE.

ELECTRIC DISINTEGRATION OF METALS AND THEIR PERIODIC GROUPING.

To the Editor of the Chemical News.

Sir,—May I allude to the work of F. Fischer and F. Schröter (*Ber. Deut. Chem. Gesell.*, xliii., pp. 1442 and 1454, abstracted in Chemical News, cii., 48) in connection with the periodic classification of the elements, since it affords, as the authors indicate, a means of classifying the metals in two groups, namely, those which disintegrate and form powders by treatment in an arc in

liquid argon (forty-five metals were examined, not counting Ru, Rh, and Os) and those which do not. The ordinary Periodic Table requires a slight modification to group the two types, which the authors show.

A periodic classification I suggested (CHEMICAL NEWS, c., 281, Table IV.) lends itself to a grouping in accordance with these results. The metals in Groups II. to VIII. inclusive—upper division of the table, including Ce, do not disintegrate. Mn is, however, an exception. The metals in Groups II. to VI. inclusive, lower division of the table, disintegrate into powders. All the metals of Group I., except Cu, disintegrate, although Au and Ag do so but slightly.

If the table is wrapped round a cylinder, so that the bottom row (VII.) is brought round next to the top row (Li, Na, &c.) the metals that disintegrate are of one block or section, and those that are stable are of another similar section. K should be regarded as filling the gap between Na and Rb. The metals of the rare earths from Pr to Lu (Cp) inclusive, have, of course, not been examined. —I am, &c.,

F. H. LORING.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cli., No. 10, September 5, 1910.

β-Rays of Radium at its Minimum Activity.—Léon Kolowrat.—When a substance containing radium is freed from the emanation and the active deposit by heating or by chemical methods, β-rays are emitted, which must come from the radium itself. The author has obtained results which confirm this conclusion, and finds that the β-radiation peculiar to radium is very easily absorbed.

Preparation of Acroleïn.—J. B. Senderens.—Potassium bisulphate acts as a dehydrating catalyser on glycerin and acroleïn is formed. Possibly potassium disulphoglycerate is formed as an intermediate product:—

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 2HKSO_4 = 2H_2O + \begin{array}{l} CH_2OH \\ | \\ CH.SO_4K \\ | \\ CH_2SO_4K, \end{array}$$

$$\begin{array}{l} CH_2OH \\ | \\ CH.SO_4K \\ | \\ CH_2.SO_4K \end{array} = 2KHSO_4 + \begin{array}{l} COH \\ | \\ CH \\ \| \\ CH_2. \end{array}$$

The yield is not quite as good as in the old methods of preparing acroleïn, but the process is economical, simple, and rapid.

Nos. 11, 12, and 13, September 12, 19, and 26, 1910.

These numbers contain no chemical matter.

Berichte der Deutschen chemischen Gesellschaft. Vol. xliii., No. 9, 1910.

Carbon Nitrogen Bond.—Heinrich Biltz.—By the study of compounds in which carbon and nitrogen are directly linked the author has found that if the basicity of the nitrogen is increased by means of suitable substituents the affinity of the nitrogen for the carbon increases, while if the acidity of the carbon is increased its affinity for nitrogen is also raised. Similar phenomena seem to occur in compounds in which two carbon atoms are directly linked.

Tantalum Sulphide.—Heinrich Biltz and Carl Kircher.—At comparatively low temperatures the action of carbon disulphide on tantalum oxide gives impure sulphide, but between 960° and 1300° preparations of constant composition are obtained, the analysis of which gives results which agree very well with the formula TaS_2. Tantalum oxide is only slightly attacked by sulphuretted hydrogen. The sulphide is quite stable up to and above 1300°, and at about 1200° begins to pass into crystals, probably undergoing slow sublimation.

Hydrazi-zinc and Preparation of Metallic Hydrazides.—E. Ebler and R. L. Krause.—When zinc methyl or ethyl acts on anhydrous hydrazine in presence of ether an unstable hydrazi-zinc of formula ZnN_2H_2 is obtained. From zinc diamide the same compound can be prepared similarly, and it has been found that many other metallic diamides react with hydrazine to give the corresponding hydrazides, which are of special interest because by their slow oxidation the diazo metals are obtained.

Atomic Weight of Tellurium.—W. Marckwald and A. Foizik.—Marckwald has found from the conversion of telluric acid $H_2TeO_4 + 2H_2O$ into the dioxide TeO_2 that the atomic weight of tellurium is 126·85, while the value given by the International Atomic Weight Commission is 127·5. Brauner oxidised TeO_2 in alkaline solution by permanganate in excess, acidified with sulphuric acid, added oxalic acid in excess, and titrated with permanganate. The value he obtained was 127·05. The author has repeated these experiments with some modifications, using iodine and thiosulphate for the back titration, and gets a result agreeing very well with that given in the International Atomic Weight Table. Possibly the values given from the conversion of telluric acid into the dioxide were too low owing to the formation of a solid solution of the telluric acid hydrate with a higher hydrate.

No. 10, 1910.

So-called Euxen-earth.—Otto Hauser and Fritz Wirth.—The examination of all the important zirconium minerals shows that zirconium earth is a single substance, and there is no indication of the existence of a similar earth accompanying it—the so-called euxen-earth. Many zirconium earths are radio-active, even when they are quite free from thorium.

Ester Condensations.—Wilhelm Wislicenus and Wilhelm Silberstein.—Oxalic ester condenses with propionitrile easily in an alcoholic ethereal potassium ethylate solution, the product being the potassium compound of propionitrile-oxalic ester, $\begin{matrix} CH_3 \\ N \end{matrix}\!>\!CH\cdot CO.COOC_2H_5$. The free ester can be obtained from the potassium compound by treatment with ice-cold sulphuric acid.

Metaphosphoric Acid Ethyl Ester.—K. Langheld.—By boiling phosphorus pentoxide for three days with excess of ether previously dried over sodium, metaphosphoric acid ethyl ester can be obtained:—$C_6H_5.O.C_2H_5 + P_2O_5 = 2C_2H_5O.PO_2$. This compound seems likely to be extensively applied in organic chemistry on account of its power of forming addition products and its condensing action.

Diazoamidotetrazolic Acid.—K. A. Hofmann and H. Hock.—In presence of free acetic acid sodium nitrite acts on amidoguanidine nitrate to give the sodium derivative of diazoamidotetrazolic acid, $HN_4C.N : N.NH.CN_4H$. This substance is a very strong tribasic acid; it is reduced by tin chloride and hydrochloric acid to give amidotetrazol and tetrazylhydrazine:—

$$HN_4C.N : N.NH.CN_4H + 4H = HN_4C.NH.NH_2 + H_2N.CN_4H.$$

MEETINGS FOR THE WEEK.

FRIDAY, 28th.—Physical, 5. Exhibition of a New Method for producing High-tension Discharges, by E. and W. H. Wilson. "Behaviour of Steel under Combined Static Stress and Shock" (with Exhibition of Apparatus); by F. Rogers.

THE CHEMICAL NEWS.

Vol. CII., No. 2657.

THE WIDE DISTRIBUTION OF SCANDIUM ON THE EARTH.

II.

By Prof. Dr. G. EBERHARD.

Although as a proof of the wide distribution of scandium I enumerated in the first part of this article (*Sitzungsber. d. K. p. Akad. d. Wissensch.*, 1908, p. 851; Chemical News, xcix., p. 30) a great number of places scattered over the whole earth in the rocks of which this element could be detected, it seemed worth while to add to their number, and also to seek for those minerals which contain scandium in large quantity. The earlier experiments had shown that in order to attain these two objects special attention must be paid to tin and tungsten ores, for scandium is very often present in thes ores, frequently in large quantity, and, moreover, they are to be found in almost all parts of the world. Thanks to the ready response with which I met on all sides it was possible for me to test for scandium the ores of almost all tin-bearing strata in the earth's crust. In the following table, which is a direct continuation of that published in Part I., all the minerals and rocks spectrographically investigated during the last two years are included. As will at once be seen from the table the conclusions stated in the first part were completely confirmed when more material was tested. Some minerals were found to contain large amounts of scandium, *e.g.*, æschynite and tin-stone from Embabaan, Swaziland, monazite and some varieties of wiikite, which Crookes showed is rich in scandium, from Impilacks in Finland, wolframite from Sadisdorf, and tin-stone from the Takayama mine in Japan. (Here the author gives a table of 459 minerals and rocks).

In 181	of them	scandium	was absent.
„ 74	„	„	doubtful.
„ 114	„	„	visible.
„ 27	„	„	visible or easily visible.
„ 38	„	„	easily visible.
„ 11	„	„	easily visible or strong.
„ 14	„	„	strong.
459			

In 237	of them	the rare earths	were absent.
„ 33	„	„	doubtful.
„ 170	„	„	present.
„ 19		„	strong.
459			

(Note.—Scandium can be detected chemically only in the minerals marked "easily visible or strong" or "strong").

Thus no mineral has been found in which scandium is an essential and not merely an accessory constituent, for wiikite cannot be regarded as such, since specimens which were all derived from the pegmatites of Impilacks, and which appeared identical, differed widely from one another as regards the amount of scandium present in them.

If those minerals in which scandium can be detected chemically are picked out, it is found that they are all derived from granites or special pegmatites (Norway, Sweden, Finland, Elba, Swaziland, &c.), for the ore veins containing tin or tungsten like those of Zinnwald, which have a thoroughly pegmatitic appearance, are included by geologists among those of pegmatitic structure (R. Beck, "Lehre von den Erzlagerstätten," 1909, I., p. 272; II. p. 54).

In 1908 Herr Vernadsky ("Zur Frage über die Verbreitung des Skandium," *Bull. l'Akad. Impériale Sciences St. Petersbourg*, 1908, p. 1273) pointed out this connection between the pegmatites and the occurrence of scandium, which I had not noticed, basing his conclusions on the results first published by me. The new material in the above table quite confirms this view.

In which minerals of the pegmatite the scandium is concentrated naturally depends upon the prevailing conditions; thus in Finnish pegmatites the scandium is found in the monazite (phosphate), in a small part of the wiikite (titanoniobate), and in the black mica, but in Swaziland pegmatite it is in the tin-stone (SnO_2) and in the æschynite (titanoniobate), while the monazite is quite free from it.

Probably it would be possible to specify more accurately the conditions for the formation of minerals rich in scandium if we determined the relation between the results which the investigation of the numerous tin and tungsten ores has given and the origin of the various tin and tungsten strata which is in the main well understood. In the description of the structure of the Eastern Ore Mountains, the geological details of which are known to me accurately enough for such a research, I shall return to this question. Some notes on the table may now be added. From a chemical point of view it must appear remarkable that scandium is contained in several sulphide ores, *e.g.*, in lead glance, copper glance, zinc blende, arsenical pyrites, fahlore from Zinnwald. The examination of pieces of these ores showed that in these cases it was not a pure mineral but one containing tin-stone, wolframite, or lithium-mica (the last usually completely decomposed so that its scandium had become concentrated). For instance, fine greenish veins of decomposed lithium-mica, arsenical pyrites, and fahlore, running through lead glance, had separated round pieces of greisen containing tin. When pure specimens were obtained for examination (which are seldom to be found in Zinnwald), scandium could not be detected (zinc blende, zinc pyrites, lead glance). The following also contain no scandium:—The sulphide tin ores from Bolivia (frankite, kylindrite), tin pyrites from St. Agnes, copper glance from the Bottalack mine in Cornwall, copper pyrites containing tin and tungsten from Niederpöbel,* arsenical pyrites containing tin from Altenberg; these are all obtained from places with tin ores containing much scandium. In this connection it is interesting to observe the behaviour of copper pyrites, which could be isolated in the pure state in small grains from wolframite containing much scandium. Both this pyrites and also a small piece of ore which formed a silver-white mineral consisting of an intimate mixture of copper pyrites and wolframite were free from scandium. In the investigation it was also found that tin ores from mines which also contain sulphide or arsenical ores are mostly free from scandium or, at any rate, contain but little of that element.

While the absence of scandium in mines yielding sulphide can be explained from a chemical point of view, there is no reason why the tin ores, the occurrence of which is connected with the pneumatolytic processes of tourmalinisation, should also contain no scandium. This is true also of the converse phenomenon, viz., the strong accumulation of scandium in wood tin from Cornwall and Bolivia, as compared with the small amount of scandium in the tin-stone and tin sulphides which are free from scandium, and which come from the same places.

After these general researches on the occurrence of scandium in the earth's crust the next question to be considered was how this element was distributed in any of the above-mentioned regions which are rich in scandium. We may regard as specially suitable for this purpose the series of post-dyassic granites which occur in a nearly rectilineal fissure between Graupen and Sadisdorf. This granite

* The presence of tin and tungsten indicates that this copper pyrites vein (Hohe Eula) owes its origin to the eruption of Sadisdorf granite as well as the tin and tungsten veins of the same place which also contain some pyrites. As specially remarkable cases may be mentioned the abundance of tin in pure bismuth from Johanngeorgenstadt and in the copper pyrites of Katharinaberg.

region of the Ore Mountains is completely surrounded by mines, which are very old but are still worked, and it has been thoroughly investigated from a geological point of view by J. Dalmer and R. Beck ("Erläuterungen zur Geologischen Spezialkarte des Königreichs Sachsen, Sections 119 and 120). The author spent several weeks in this region in 1908 and also in 1909 (aided by a grant from the Academy), and collected much material in the way of of rocks and stones.

The geological structure of this region of the Ore Mountains is composed of the following formations and rocks:—

I. Gneiss Formation (Upper and Lower Gneiss).
II. Phyllite Formation.
III. Coal Formation.
IV. Older Eruptive Rocks (Teplitz Quartz Porphyry, Granite Porphyry, Granite.
V. More Recent Eruptive Rocks (Basalt).

Of these rocks the different gneisses, especially those in Zinnwald, contained a small but normal amount of scandium, the carbonaceous porphyry, tuff, Arkose sandstone, as well as the allied black granite porphyry of Schellerhau, and the lode porphyries an almost imperceptible amount, and the phyllites a relatively large amount. In the granite porphyry and the Teplitz quartz porphyry the amount of scandium present seems to depend upon the amount of mica; the granitic granite porphyry, which is quite free from mica, contains no scandium; but even varieties which are rich in mica are poor in scandium. But all these rocks (with the exception of the phyllites) are known in the pneumatolytically altered condition* (Zwitter), and the course of the metamorphic process does not seem to determine in which pieces in the neighbourhood of the granite containing scandium the scandium will accumulate. (The accumulation is usually only slight). Thus scandium, like silica, tin, lithium, fluorine, &c., migrates into the rocks on weathering. It might be thought that the chemical processes occurring during weathering caused merely a concentration of the scandium originally present in the rock; but this is certainly not correct in most cases. The behaviour of Teplitz quartz porphyry is specially instructive in this connection; it is rich in crystals in Zinnwald, and, except for occasional clusters of mica, seems to contain only very little of this mineral, so that scandium cannot always be detected with certainty in the unattacked rock, and thus *a priori* a concentration of scandium occurring during weathering is improbable.

I have examined a very much changed quartz porphyry which directly bordered on a vein of tin-stone, and I found that it had not only become very rich in lithium and tin, but that scandium had also accumulated relatively abundantly. If this accumulation had occurred owing to the concentration of a mineral originally present in the rock, a piece obtained at a great distance from the vein, which in consequence of very slight chemical action had quite preserved its quartz porphyritic structure, must be poorer in scandium than that which is much affected. But this is not the case. Moreover, the porphyry from Gultenschacht in Zinnwald, which has become almost unrecognisable owing to weathering, as well as the much changed pieces from Seegrund, must contain much less scandium than the far less strongly affected well-preserved pieces. On the contrary, the former contain much more than the latter. It is still more convincing that the only slightly affected quartz porphyry occurring between two bands of zwitter, which themselves were much changed, shows the same amount of scandium as these bands. In the weathering of Teplitz quartz porphyry, especially when it is in contact with granite, undoubtedly a migrating of the scandium occurs from outside just like that known to occur with lithium. Thus there is a certain analogy between these two elements as regards the migration. Thus almost invariably weathered rocks of whatever kind become richer in lithium and scandium if they are obtained from the neighbourhood of a metallic vein, of an impregnation or of granite, than if they have been taken further from these places by increased pneumatolytic activity. This also explains why the weathered quartz porphyry of Seegrund which occurs at a great distance from Zinnwald granite contains neither lithium nor scandium; that lying nearer the granite contains both elements, if in small quantity only; while the pieces from the neighbourhood of a tin-stone vein are very rich in lithium and nearly equally rich in scandium. If the granite contains no scandium the older altered rocks, especially the weathered quartz porphyry, are also free from it, as, for example, that from Raubschloss, which owes its metamorphosis to the granite of Preisselberg, near Graupen, which is free from scandium or contains only very little of it. It cannot be definitely stated how the migration occurs. It is almost always assumed that when tin ore deposits were formed, especially in the region of Zinnwald, gases or solutions containing fluorine acted, and in the weathered quartz porphyry containing scandium fluorine is present (as fluorite), but scandium fluoride is insoluble at any rate under laboratory conditions, and is volatile only at the high temperature of the arc. Thus in impregnation with scandium the action of fluorine can be regarded only as the second act of impregnation, rather like the fixation of already migrated scandium. In passing it may be mentioned that the impregnation of rocks around the Zinnwaid granite is not of the same nature; it has already been stated that lithium and scandium are more sparingly deposited the further the place is from the ore veins or the granite. On the other hand, silicon, fluorine, and tin occur at much greater distances. Thus it is known that some tin mines at Seegrund near Zinnwald gave a good yield of tin, and also the weathered granite porphyry from Zinnwald, which is free from lithium, contains several per cent of tin.

The impregnation regions round the other granites from this district show still greater varieties—silicication, chlorination, weathering, with migration of lithium. All these processes can be connected either with an abundant or slight migration of tin. In the above table there are many examples of this vast and much too little studied natural manifestation of chemical activity.

The granites between Graupen and Sadisdorf behave in practically the same way as the rocks treated above. We need only specially mention here the characteristics which the Zinnwald granite shows, as these can readily be recognised and are typical of the granites of this region.

Zinnwald granite contains scandium in the perfectly fresh parts, as they are to be found usually only in apophyses. It is contained in the mica and the minerals of the granite, as it cannot be detected by spectrographic analysis either in the quartz or the felspars, particularly the orthoclase containing tin. Whether it occurs in the mica minerals themselves, or in the little particles of ore contained in the mica, cannot be decided.* But probably the last assumption is correct, as strongly decomposed micas are both rich in tin and fairly rich in scandium. The petrographically different granite formations which appear in Zinnwald show no essential differences as regards the scandium contained in them, and, moreover, there seem to be no more marked local differences. Specimens of the granite masses taken from different places are almost equally strongly infected.

The amount of scandium in the greisen obtained from Zinnwald granite also depends upon the amount of ores and mica in the rock. Thus, pieces which came from the neighbourhood of a metalliferous vein are richer than those which were obtained at some distance from it. This shows

* It makes no difference whether pneumatolytic or hydrothermic change, or both, have taken place. To avoid repetition the expression "pneumatolytic" is always used.

* Sadisdorf and Altenberg greisens show scandium only faintly if they (as usual) contain a fair amount of tin, but fairly strongly if they are rich in tin. Also in the tin-stone from normal greisen from both places it appears strongly. These observations show that the scandium of both these granites is usually, at any rate, contained in the tin-stone.

that, as in granite, the scandium is contained in the ores and in the mica. But these minerals owe their origin to the expulsion of hot solutions or gases containing metals, and accompanying the granite eruption. There is therefore no doubt that, like the other metals (tin and tungsten), scandium has reached the earth's surface from the magma by similar processes, which is confirmed by the fact that the study of quartz porphyry led to the same conclusions. Possibly in the last named rock the scandium was connected with the tin-stone and with the lithium mica. Unfortunately, it cannot yet be decided in what combination the element is present in the ores, otherwise we could draw further conclusions. The scandium is fairly uniformly distributed in the ores, as specimens taken from different places show. As an exception, it appears to occur sparingly in the tin-stone of a vein in quartz porphyry, and in a tin-stone concretion in the quartz porphyry itself—the latter is not connected with a vein. In the weathering of wolframite it is concentrated in the tungsten ochre finally remaining. It is also present in large quantities in some ores of more recent date, especially in scheelite ("Erläuterungen," p. 92). Possibly scheelite has arisen from a transformation of the wolframite, as in Zinnwald pseudomorphoses of scheelite are found near wolframite.

With regard to the scandium contained in the other allied granites, we may mention that the minerals of the Sadisdorf granite are as rich as those of Zinnwald, but the tin-stone of the Paradies mine in the Schellerhauer granite and the tin-stone and wolframite of Altenberg granite contain less, and the tin-stone of Bärenstein still less. The conditions of the Graupen district have not yet been sufficiently explained, for the ores of some lodes contain it in the same amount as those at Altenberg, while the ores of other localities are almost free from it; *e.g.*, the tin-stone of Preisselberger Pinge.

In any case the ores of the granites between Graupen and Sadisdorf are distinguished by their amount of scandium from those of the other granites of the Ore Mountains (Geyer, Ehrenfriedersdorf, Abertham, Hirschenstand, Breitenbrunn, Schlaggenwald, Tirpersdorf), and of the Fichtel Mountains.* For in these scandium is present at the most only in the quantity in which it almost always occurs. From this fact it must be concluded that the granites between Graupen and Sadisdorf arose from a single magma crater, even if they and their impregnation regions are not very much like one another.

It was possible to carry out this research only by the application of the direct spectrographic examination of rocks and minerals. This method can always be applied with advantage, if one wishes to find out quickly and easily the qualitative composition of a mineral or rock, for which either there are no good chemical reactions (*e.g.*, the acid earths), or which are present in too small quantities to be detected chemically. Petrographic and, still more, chemical analysis can, of course, never be quite replaced by spectrographic analysis.

Note.—In this research the general distribution of titanium, vanadium, copper, and strontium in the earth's crust was proved, and further it was found that almost all eruptive rocks of the Ore Mountains, even if they are not connected with tin-stone deposits (*e.g.* gneiss, quartz porphyry, granite porphyry), even basalt contain a small amount of tin (the last named owing to the fusion of older rocks containing tin).

It only remains for me to express my thanks to all those gentlemen who have aided me in my research by sending me rocks and ores, especially to Herr S. Pels, of Hamburg, Herr Schiller, of Graupen, Dr. Schröder, of Gera, who sent me many sets of specimens. I am particularly grateful to Dr. R. Beck, of Freiburg, who not only sent me valuable specimens, but also examined a great number of rocks petrographically, and always gave me most willingly his valuable expert advice.—*Sitzungsber. d. K. p. Akad. d. Wissensch.*, 1910, xxii., 404.

* In the greisen formation in the E. Ore Mountains, from Markersbach to Geyer and Ehrenfriedersdorf inclusive, lithium always accumulates (in comparison with the original granite), but in the granites of the W. Ore Mountains and the Fichtel Mountains the greisen contains less lithium than the granite.

COLLECTION OF COLLOID PRECIPITATES.

By MORTON LIEBSCHUTZ.

I have thought it may interest some of your readers to have their attention called to the following.

My work as analytical chemist of the Balbach Smelting and Refining Company of Newark includes brass and bronze analysis. It is often required to have rapid determinations of tin made, the amount of which runs around 2 per cent. Working on 10 grms. of drillings I had great trouble in preventing the metastannic acid (obtained in heating drillings in dilute nitric acid) of passing through my filters, and I suppose other analysts are in the same predicament.

But if to the solution, in which the colloidal metastannic acid remains suspended, I add a dilute solution of albumin and heat for a short while, the albumin coagulating carries down the tin as a curd, which can be filtered off at once. The rest of the analysis proceeds as usual. It is necessary, however, to get rid of the copper retained by the metastannic acid by washing back the precipitate of tin and albumin into the beaker, and boiling for a little while with dilute nitric acid. The filtrate is perfectly clear, and thus my bugbear of filtering metastannic acid has been overcome.

I use a similar principle for the rapid separation of zinc from copper when separating zinc by the cyanide method. The gelatinous zinc sulphide is very difficult to wash after the copper cyanide has been separated by decantation from the zinc sulphide. But if to the solution in which the zinc sulphide is in suspension I add a few drops of a solution of lead acetate, the lead sulphide formed carries down the zinc sulphide, and filtration can proceed at once, giving a perfectly clear filtrate. The mixture of zinc and lead sulphides is then treated by dilute HCl, boiled for a short while, and zinc titrated as usual by ferrocyanide of potassium. By this scheme determination of zinc in copper electrolytes can be carried in about ten minutes. No doubt that the albumin method first mentioned could be used advantageously for the coagulation of precipitates other than metastannic acid and their rapid filtration.

Newark, New Jersey, September 28, 1910.

LEAF DECAY AND AUTUMN TINTS.

By P. Q. KEEGAN, LL.D.

In *Nature*, vol. lxix., No. 1776, p. 30, I endeavoured to show how, inasmuch as the leaves of our forest trees at the period of the autumnal shedding were not similar as respects their condition of vitality, the relation between the individual stages of vitality attained by the various species and the particular hue or tint (red, yellow, or brown) which they assume in autumn, may be demonstrated by a comparison of certain of their ash constituents. The connection between vitality and coloration may, however, be explicitly exposed in other ways. The most direct and pregnant method would doubtless be that which endeavoured to trace out and follow up the course or march of the albumenoids which minister directly to the vitality of the protoplasm. This can, I think, be done. As a matter of fact, it so happens that in a certain number of species the quantity or ratio of the albumenoids of the leaf remain permanent from about July till the time when the chlorophyll commences to fade and disappear, while again in a certain number of other species this quantity or ratio becomes gradually and permanently less. For

instance, in the leaves of hazel, sycamore, horse chestnut, alder, willow, elm, hornbeam, vine, &c., the proportion of nitrogenous substances does not diminish as the leaves grow old; whereas in plane, mulberry, poplar, wild cherry, rowan, beech, scarlet oak, larch, birch, robinia, hawthorn, elder, dogwood the proportion does diminish, and in some instances very decidedly so. A few instances are here given in the following table:—

	Albumenoid in summer.	Albumenoid in autumn.
Leaves Red in Autumn.		
Wild cherry ..	6·5	0·76
Rowan	11·3	3·4
Birch..	11	6·1
Elder..	14·7	8·8
Leaves Brown in Autumn.		
Oak	14·4	7
Sycamore.. ..	20·3	20
Hazel	17·3	16
Beech	19·3	7·3
Elm	17·9	16
Alder..	9·2	18·7

The figures represent the percentages in the dried leaf.

It will be observed that of the browning leaves the oak and beech are occasionally bright red, and hence, as indicated, the proportion of albumenoid in their case alone suffers a diminution in autumn. The physiological causes of these differences is, that in the one set of cases the vegetation of the tree terminates earlier than in the other cases, and hence the organic principles, already formed and apt for chemical transformations, having got nothing more to do, as it were, remain permanent, and tend to accumulate relatively to the other constituents.

This circumstance suggests the chemical origin of the red colouring matter (erythrophyll). It suggests the idea that there is a close connection between the diminution of the albumenoid matter and the development of the vivid crimson, purple, &c., coloration. In fact, the withdrawal of the albumenoid induces, or is the result, of an energetic process of deassimilation, *i.e.*, a disruption of the albumenoid molecule, especially of the epidermal cells of the leaf, a separation of its nitrogenous nuclei, and a relinquishment of its aromatic nuclei, which latter would be left behind as chromogens of red pigments more or less vivid and pure. It has been considered by some physiologists that the albumenoid so withdrawn is conveyed to other parts of the tree, to be there employed or to be stored up for future employment. This assumption, in my opinion, is quite unnecessary. In the declining vitality of the foliar organ incident to the approach of autumn, the energy necessary to the sustenance of albumenoid activity is not forthcoming, and hence a process of deassimilation readily ensues. On the other hand, in those trees where the vegetation is exhausted, the albumenoids remain stored up as a sort of reserve with no stimulus to transform or deassimilate into chromogen.

Patterdale, Westmorland.

Electric Vacuum Furnace.—Otto Ruff.—The author describes an electric vacuum furnace with a carbon tube which may be used as a carbon tube resistance furnace for performing operations *in vacuo* or in absence of atmospheric air. In the furnace vanadium can be prepared from its trioxide by reduction with carbon, and by its use it has been found that alumina, magnesia, and lime are much more fusible and volatile than is generally supposed. Even below the melting-point their volatility is such that no trace of fusion could be observed. The furnace can conveniently be used as an arc furnace.—*Berichte*, xliii., No. 9.

THE TRANSFORMATION OF NITROAMINES AND ALLIED SUBSTANCES, AND ITS RELATION TO SUBSTITUTION IN BENZENE DERIVATIVES.*

(Concluded from p. 205).

Measurement of the Speed of the Opposing Reactions in the Equilibrium—

$$k_{II}[Ar.NHAc][Cl_2] = k_{III}Ar.NClAc] + [HCl]^2.$$

SINCE the action of chlorine on acetanilide is very rapid the chlorination of acetanilide by a chloroamine and hydrochloric acid gives a means of determining the value of the co-efficient k_{III} and since k_{II}/k_{III} is known also the value of k_{II}. When the concentration of acetanilide is so large that the velocity of the chlorination is not increased by further rise in the concentration of the acetanilide, it is obvious that the speed of the total change is controlled by that of the interaction of the chloroamine and hydrochloric acid, the slowest step in the series. That is the speed of the chlorination $= k_{III}$[chloramine].[HCl]^2. The chloroamine alone varies in concentration, hence the velocity of the reaction is expressed by an equation of the first order. For two determinations of the amount of chloroamine, p and q, at times t and t_0, we have therefore –

$$k_{III}[HCl]^2 = \frac{1}{t - t_0} \cdot \log e \frac{p}{q} = \lambda;$$

or—

$$k_{III} = \lambda/[HCl]^2.$$

The values of k_{II} and k_{III} are shown for a number of anilides in Table IV.

TABLE IV.

Anilide.	Medium. Dilute acetic acid.	k_{111}.	K.	k_{11}.
p-Nitroacetanilide .	50 per cent	109	—	—
p-Chloroacetanilide	50 ,,	4·6	—	—
p-Chloroacetanilide	65 ,,	22	8·1	178·2
2 : 4-Dichloroacetanilide	50 ,,	15·5	[69·8?]	[1081?]
	65 ,,	91	4·47	406·8

The Interaction of Acetanilide with Acetylchloroamino-p-chlorobenzene and Hydrochloric Acid.—The effect of the presence of an anilide on the conversion of the corresponding chloroamine—for example, of acetanilide on the conversion of acetylchloroaminobenzene, or of *p*-chloroacetanilide on that of the acetylchloroamino-*p*-chlorobenzene—is small. In the first instance, owing to the equilibrium, the concentration of the chloroamine is increased and that of free chlorine reduced. But in 50 per cent, or even in 65 per cent, acetic acid, the proportion of free chlorine and anilide is so small, that relatively little alteration of concentration of the chloroamine is brought about, but the alteration in the chlorine is considerable. Thus, taking as an example the system made up from *p*-chloroacetanilide and chlorine, the proportion of free chlorine is 0·4 and 5·3 per cent in 50 and 65 per cent acetic acid respectively, but on adding one molecular proportion of the anilide this drops to about 0·2 per cent in the latter medium. The velocity of chlorination increases in the ratio 1·19/1 in 50 per cent, and in the ratio 1·22/1 in 65 per cent. With acetanilide, where the proportion of free chlorine is somewhat less, the ratio of the velocities is 1·13/1.

When acetanilide and the chloroamine of *p*-chloroacetanilide interact in the presence of hydrochloric acid the result is very remarkable and instructive. The acetanilide is alone chlorinated; the amount of 2 : 4-dichloroacetanilide is insufficient to admit of detection. On comparing the velocities the remarkable character of the reaction is made more clear. In 50 and 65 per cent acetic acids the reactions are of the first order.

* Report of the Committee, consisting of Prof. F. S. Kipping (Chairman), Prof. K. J. P. Orton (Secretary), Dr. S. Ruhemann, Dr. A. Lapworth, and Dr. J. T. Hewitt. Read before the British Association (Section B), Sheffield Meeting, 1910.

	k_1 in 50 per cent.	k_1 in 65 per cent.
p-Cl.C_6H_4.NClAc + HCl → 2 : 4-Cl_2.C_6H_3.NHAc	0·00053	0·0023
C_6H_5.NClAc + HCl → o- and p-Cl.C_6H_4.NHAc	0·00039	0·0026
p-Cl.C_6H_4.NClAc + HCl + C_6H_5.NHAc → o- and p-Cl.C_6H_4.NHAc	0·0016	0·0092

In both media the speed of chlorination of acetanilide by the chloroamine of p-chloroacetanilide is far more rapid than the conversion of the chloroamine of acetanilide into the isomeride. In 50 per cent acetic acid the conversion of acetyl chloroamino-p-chlorobenzene is faster than that of acetylchloroaminobenzene. Although the experiments on the changes occurring when an anilide is added to a mixture of the chloroamine of another anilide and hydrochloric acid, show that in this case the chloroamine of acetanilide may be formed, yet the relation of the velocities of the C-chlorination in the various systems make it impossible for the chlorination of the acetanilide to take place by way of the chloroamine. If that were the route, the process could not be faster than when the starting-point was the chloroamine of acetanilide. Further, when on the other hand the chloroamine of acetanilide and hydrochloric acid interact with p-chloroacetanilide in 50 per cent acetic acid, a slow chlorination occurs, and in spite of the difficulty of isolating small quantities of 2 : 4-dichloroacetanilide from such a mixture, its presence was undoubtedly demonstrated by the isolation of the pure material; that is, some chlorination of p-chloroacetanilide took place.

Mechanism of Chlorination (and Bromination) and of the Conversion of Chloroamines.

The experiments recorded in the foregoing leave no doubt that the chloroamines cannot be regarded as even occasional intermediaries, much less necessary intermediaries in chlorination. They would rather appear to be by-products. (They can only be regarded as intermediaries when hypochlorous acid acts on an anilide, for then the chloroamine only and no C-chloro-derivative is formed. Introduction of hydrogen chloride is required, however, for the conversion of the chloroamine into the C-chloro-compound).

The residual valency of the nitrogen atom was urged by Armstrong as the prime factor in bringing about the initial union of the substituting agent and the anilide. Such a substance would be, in chlorination, the compound, $Ar.NHAcCl_2$, identical with the complex formed from chloroamine and hydrochloric acid, already referred to.

If the existence of this reactive complex be assumed, our experiments enable one to deduce a number of its properties.

(i.) The action of chlorine on acetanilide and p-chloroacetanilide in various dilutions of acetic acid, show that the rate of formation and of change of the complex into the substituted anilide must increase rapidly with dilution of the acetic acid.

(ii.) The concentration of the complex (in any case minute) must rapidly decrease with dilution of the acetic acid medium, in a system which has attained equilibrium, since the velocity of C-chlorination in a system prepared from chloroamine and hydrochloric acid decreases with the dilution.

(iii.) Inasmuch as the rate of C-chlorination in diluted acetic acid is so markedly faster when chlorine and anilide are allowed to interact than when the system is prepared from chloroamine and hydrochloric acid, the rate of change of the complex into a C-chloro-derivative must be greater than into the N-chloro-derivative :—

$$Ar.NHAcCl_2 \xrightarrow{\text{slow}} Ar.NClAc + HCl$$
$$Ar.NHAcCl_2 \xrightarrow{\text{fast}} ClAr.NHAc + HCl$$

On the other hand, in acetic acid of high concentration, 90-100 per cent, the rate of change of the complex into chlorine and anilide must be much faster than into chlorinated anilide :—

$$Ar.NHAcCl_2 \xrightarrow{\text{slow}} ClAr.NHAc + HCl$$
$$Ar.NHAcCl_2 \xrightarrow{\text{fast}} Cl_2 + Ar.NHAc$$

for the rate of C-chlorination is the same whether the system is made up from chloroamine and hydrogen chloride or from chlorine and anilide.

(iv.) The complex formed from acetanilide may be compared with that formed from p-chloroacetanilide. Since the speed of chlorination of acetanilide is very much greater (200 times in glacial acetic acid) than that of p-chloroacetanilide, the rate of formation of the complex from acetanilide and of its transformation are the more rapid. Nevertheless in dilute acetic acid, 50 per cent, the rate of conversion of acetylchloroaminobenzene (k_1=0·00039) is slower than that of acetylchloroamino-p-chlorobenzene (k_1 = 0·00053); hence it must be assumed that the complex is produced at a slower rate from hydrogen chloride and acetylchloroaminobenzene, or, what would have the same effect, its concentration is very much smaller than in the case of p-chloroacetanilide. Moreover, the contrast is emphasised by the fact that the speed of chlorination of acetanilide by the chloroamine of p-chloroacetanilide is relatively high. Here it must be assumed that the very fast formation (and re-arrangement) of the compound of acetanilide and chlorine, the latter being set free by the reactions :—

$$p\text{-Cl.}C_6H_4\text{.NClAc} + HCl \rightarrow Cl.C_6H_4NHAcCl_2 \xrightarrow{\text{slow}} Cl_2.C_6H_3.NHAc + HCl$$
$$Cl.C_6H_4NHAcCl_2 \xrightarrow{\text{fast}} Cl.C_6H_4.NHAc + Cl_2$$

keep the concentration of the compound, $Cl.C_6H_4.NHAcCl_2$, at vanishing point and thus prevent the formation of 2 : 4-dichloroacetanilide.

Alternative Hypothesis. Direct Action of Halogen on Anilide or on a Dynamic Isomeride.

It may well be asked whether the facts of chlorination and the transformation of the chloroamines require for their interpretation the assumption of the existence of a complex with many-sided characters and capable of undergoing an intramolecular re-arrangement in which the wandering group is a chlorine atom.

The specific part played by the hydrogen chloride in the transformation of the chloroamine, and the fact that this reagent causes the production of chlorine and anilide, and the results of numerous experiments, which may be summarised in the statement—whenever chlorine and anilide are present at maximum concentration the speed of chlorination is highest—are more or at least as simply accounted for by direct interaction of chlorine and anilide.

An example may be found in the relation between the rate of conversion of the chloroamine and the concentration of the hydrogen chloride. Blanksma showed for acetylchloroaminobenzene that the reaction was of the first order, and the velocity proportional to the square of the concentration of the hydrogen chloride. Assuming the conversion to be due to the setting free of chlorine and anilide followed by direct chlorination, then—

$$d[\text{chloroanilide}]/dt = k_{II}[\text{anilide}][Cl_2].$$

But

$$K[\text{anilide}][Cl_2] = [\text{chloroamine}][HCl]^2;$$

hence

$$d[\text{chloroanilide}]/dt = k_{II}[\text{chloroamine}][HCl]^2/K$$

[chloroamine] equals approximately the chloroamine

originally present, when the amount of anilide and chlorine in the system in equilibrium is very small, as in the case in media below 50 per cent acetic acid. [HCl] is constant. Hence—

$$d[\text{chloroanilide}]/dt = k_{II}.\text{Const.}[\text{chloroamine}]/K = k'$$

[chloroamine], a reaction of the first order.

But it still remains to suggest causes for the extraordinary reactivity of anilides towards substituting agents and their rigid adherence to the ortho-para law. The hypothesis may be put forward that the constitution of anilines and anilides, similar to but in a less degree than *p*-nitrosophenol, permits of the passage into a dynamic isomeride of quinonoid structure, which is accompanied by the wandering of hydrogen of the imino group to the *o*- or *p*-position. It is this isomeride which is reactive. The almost exclusive occurrence of *o*- and *p*-quinonoid compounds accounts for the position taken up by the substituting group. Just as with the hypothetical intermediary complex, a change of structure of the benzene nucleus is assumed; but here the mobile hydrogen atom and not chlorine migrates.

Further, this suggestion brings out the close analogy of the anilines and anilides with the phenols, where there is little evidence for the formation of compounds of the substituting agent with the oxygen, and much other evidence for the occurrence of a quinonoid structure.

This suggestion, on the other hand, relegates to the background the attractive view of the part played by the latent valency of the tervalent nitrogen, which permits of a ready means of primary union between the substituting agent and the anilide.

Flürscheim (*Journ. Prakt. Chem.*, 1905, [2], lxxi., 497; 1907, [2], lxxvi., 165) has attempted to account for the laws of substitution in aromatic compounds by reference to latent or rather partial valencies of certain of the carbon atoms in a monosubstituted derivative of benzene; with certain substituents the attractions on the hydrogen atoms in the *o*- and *p*-positions, and with others in the *m*-position are loosened, and hence more readily re-substituted. It is obvious that this view is independent of intermediate compounds, and would harmonise generally with the facts of chlorination as recorded in the foregoing.

Recently Lowry has discussed this subject (*Science Progress*, 1909, iii., 616; iv., 213), and has suggested various ways in which the facts may be accounted for. He points out that the migrating group is always present in the system, whenever isomeric change is taking place.

II.—*Bromination of Anilides and the Conversion of Bromoamines.*

(With W. J. Jones, B.Sc.).

The interaction between bromoamines and hydrobromic acid only differs in degree from that between chloroamines and hydrochloric acid. Tintometric measurements have shown that in acetic acid of all dilutions the reaction is quantitatively:—

$$\text{Ar.NBrAc} + \text{HBr} = \text{Ar.NHAc} + \text{Br}_2.$$

The direct bromination of the anilide is therefore always identical with the conversion of a bromoamine under the influence of hydrobromic acid.

The bromination which results when a chloroamine is treated with hydrogen bromide (or a bromoamine with hydrogen chloride) is a far more rapid process. In both these cases bromine chloride is formed and is the brominating agent.

Bromination, however, differs in one respect very markedly from chlorination in that hydrobromic acid and bromide exert a powerful retarding influence. Thus in the presence of four molecular proportions of hydrobromic acid, bromine does not act on acetanilide in glacial acetic acid at 16°. Hydrochloric acid, even when present at 8—10 times the concentration of the chlorine, has a scarcely perceptible effect.

The bromide exerts its maximum effect in glacial acetic acid. Addition of water reduces the effect, and as Fries has shown (*Annalen*, 1906, cccxlvi., 128), dilute acetic acid is the best medium for bromination of anilides. Thus in one of our experiments, in 75 per cent acetic acid, using the molecular ratio, $8HBr : Br_2 : C_6H_5.NHAc$, three-quarters of the acetanilide was brominated in twenty minutes. *p*-Chloroacetanilide in glacial acetic acid is brominated too slowly for easy measurement; in 50 per cent acetic acid, $k_{II} = 0{\cdot}36$, and in water = 12.

The cause of this influence lies in the union of the bromine with bromidion forming Br'_3. We have shown by the method of aspiration that in glacial acetic acid, when bromine and hydrobromic acid are in molecular proportions, 75 per cent of the bromine is combined with bromidion, but as the acetic acid is diluted the percentage of free bromine rapidly increases. In water we obtained by our method for the equilibrium, $K = [Br_2][Br'][Br'_3]$, values similar to those found by Jakowkin (by measurement of the distribution ratio between water and carbon tetrachloride) (*Zeit. Phys. Chem.*, 1896, xx., 38): our value for K_{15° is 0·62, and Jakowkin's $K_{25^\circ} = 0{\cdot}63$.

FURTHER OCCURRENCES OF TANTALUM AND NIOBIUM IN WESTERN AUSTRALIA.*

By EDWARD S. SIMPSON, B.E., F.C.S.,
Government Mineralogist and Assayer of West Australia.

At the Adelaide meeting of the Association, in 1907, I had the honour to present a paper embodying all the then available information with regard to the occurrence of tantalum and niobium in Australia. While no new finds of minerals containing these metals in the Eastern States have come under my notice in the meantime, a considerable amount of further information has been collected with regard to West Australian occurrences, which it is the object of this paper to describe.

Until quite recently it was a matter of impossibility to separate occasional fragments of black tantalates and niobates from parcels of black stream tin except where they showed well-developed crystal faces or other prominent characteristics. The publication, in Vol. viii., of the *Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, of Prof. G. H. Stanley's "New Test for Cassiterite," has very materially altered the aspect of affairs. This method is invariably used by the author in his examination of tin ores for rare minerals. A shallow dish about 4 inches by 3 inches is made by turning up the edges of a piece of stout sheet-zinc; in this are placed the concentrates in the form of sand or coarse fragments up to ¼ inch diameter, and then covered with dilute (5E) hydrochloric acid. In about one or two minutes the acid is poured off and replaced with water, when all fragments of cassiterite which have been in contact with the zinc are found to be coated with a bright deposit of metallic tin, so that they can easily be picked out, leaving a residue of other minerals which are not appreciably affected by the short immersion in dilute acid. This residue is submitted a second time to the same process, as possibly it may contain some fragments of cassiterite which are not coated because they have not been in contact with the zinc. After drying the final residue, it is freed from magnetite with a hand magnet, and if necessary from ilmenite by a weak electro-magnet. Hand-picking will remove quartz, monazite, &c. The final residues are then examined by chemical and physical tests for the tantalum minerals, tantalite, euxenite, &c.

If the method here outlined were applied to all samples of tin concentrates in the possession of members of the Association, it is possible that our knowledge of the distribution of tantalum and niobium in Australia would be greatly extended.

* A Paper read before the Australasian Association for the Advancement of Science, 1909.

Moolyella.—In my previous paper mention was made of the recognition of two small pieces of mangano-tantalite in Moolyella stream tin ore, whilst it was suggested that in such material others might easily be overlooked. During the collection of exhibits for the Franco-British Exhibition some most interesting bulk samples of concentrates came to hand from Moolyella. One was marked "Sluice-box residues, Macdonald's Lead," and subsequent inquiries elicited that it was representative of the lighter waste material obtained by re-sluicing the first concentrates obtained from the sluicing of alluvial tin wash. These "residues" were somewhat coarse grained, the particles averaging about 3 mm. in diameter, and only 0·2 per cent passing a 10-mesh screen. A separation effected on the lines described above showed its composition to be—

	Per cent.
Cassiterite	26·3
Monazite	26·2
Garnet	1·0
Columbite	46·5
	100·0

The chief base present in the columbite is manganese. The average specific gravity is 6·1, indicating the presence of about 40 per cent of tantalic oxide and 43 per cent of niobic oxide. The mineral is opaque and black in colour, and rather dull on the surface. The majority of the fragments are quite irregular in outline, but a large number are in flattened pieces, in which the faces XX, *a*, and a^1 are well developed. Faces *b*, *c*, and possibly *u* are imperfectly seen.

Columbite having been found in such profusion in this material, a search was made for it in three one-hundredweight parcels of stream tin concentrates from the Moolyella district. The first was from Moolyella proper, the second from Tadgebanna, the third from Mud Springs. The following results were obtained:—

	Moolyella.	Tadgebanna.	Mud Springs.
Size—Refused 20 mesh	67·0	89·4	96·3
Passed 20 mesh	33·0	10·6	3·7
Metallic tin by wet assay (per cent)	61·08	61·21	65·17
Tantalic and niobic oxides (per cent)	12·34	10·86	6·95
Equal to columbite (per cent)	15·5	13·5	8·5

Some of the carefully separated columbite was found to be identical in appearance with that obtained from the "Sluice-box residues." One unusually large fragment had a specific gravity of 5·80 corresponding to a mangano-columbite with 26 per cent of tantalic oxide and 56 per cent of niobic oxide. Associated with the cassiterite and columbite were small proportions of an almost colourless garnet, monazite, magnetite, quartz, and in one case albite.

Cooglegong.—This continues to maintain its reputation as a mineral field of exceptional interest. In my previous paper reference was made to the occurrence at this spot of euxenite, monazite, and gadolinite. I have now to record further the occurrence of fergusonite for the first time in Australia. A parcel of alluvial material recently forwarded to me from Cooglegong, and described as coming from a gully on the sides of Trig Hill, was found to consist wholly of this mineral in a more or less weathered state. Individual fragments varied from about ¼ grm. up to 6 or 7 grms. in weight. They were mostly angular pieces devoid of crystalline form, but some were somewhat fan-shaped imperfect crystal aggregates. Externally the pebbles were mostly dull and covered with a brownish red or grey adherent coating, consisting of decomposition products. On a fresh fracture the mineral is brownish black and brilliantly vitreous. It is opaque except in very thin splinters under the microscope, when it is transparent, colourless, or very pale greenish brown in colour, and completely isotropic. This latter characteristic is of considerable interest, and has not been previously recorded. Normally the mineral being tetragonal is anisotropic. An analogy, however, is found in other minerals containing the rare earths, viz., gadolinite, thorite, and allanite, all of which are normally anisotropic, but become by alteration abnormally isotropic. The powder is light ash-grey in colour.

The specific gravity of various fragments differed considerably, the following values being obtained:—5·82, 6·01, 6·24, 6·48, 6·65. This variation may be due either to differences in the water content, or to differences in the relative proportions of tantalic oxide and niobic oxide. A crystalline fragment weighing about 6 grms. was selected for analysis and coarsely crushed, all particles showing weathered surfaces being then rejected. The unweathered portion remaining had a specific gravity of 6·236 at 22·9°, and a hardness of 6. Before the blowpipe it was infusible, and did not decrepitate or glow, but turned light yellow in colour. In the close tube it yielded water. On crushing it yielded a greyish white powder. Its composition was:—

Fergusonite, Cooglegong.

	Per cent.	Molecules.
Tantalum pentoxide	55·51	12·5
Niobium pentoxide	2·15	0·8
Titanium dioxide	2·20	2·7
Tin dioxide	nil	—
Thoria	1·02	0·4
Yttria	23·00	10·2
Erbia	8·38	2·2
Ceria	0·94	0·3
Lime	2·18	3·9
Iron protoxide	trace (*a*)	—
Manganese protoxide	0·87	1·2
Uranium trioxide	1·18	0·4
Ignition loss (mainly water)	3·36	18·7
	100·79	

(*a*) Less than 0·10 per cent.

The water is evidently an alteration product, and probably varies in different parts of the one specimen. Neglecting this, we get the usually accepted formula for fergusonite, viz., $R_2O_3.Ta_2O_5$.

This particular example of fergusonite differs from all others hitherto described in two interdependent factors, viz., in its high specific gravity and in the very high proportion of tantalum relatively to niobium. It is probably one of the two minerals "allied to euxenite in physical characteristics" alluded to by Mr. B. F. Davis.

The mineral collection of the Perth Museum having now been amalgamated with that of the Geological Survey, opportunity has occurred for examining in detail the parcel of euxenite in the former collection referred to in my 1907 paper. This parcel was found to consist (except for three fragments) of euxenite in angular pieces from half a grm. up to 57 grms. in weight. Several showed indistinct traces of crystal faces. Associated with the euxenite was one piece of cassiterite and two of gadolinite. The locality of this specimen is undoubtedly Cooglegong, and it is alluvial in origin. The surfaee of the mineral is dull and brown in colour from decomposition. On a fresh fracture it has a brilliant resinous lustre, and is olive-brown in colour. On wetting, the colour is seen to be somewhat mottled, varying from light to dark olive-brown. In mass it is opaque, but in a powder under the microscope it is transparent, light brown, and, like the fergusonite, isotropic. Its hardness is 7, and specific gravity 5·1 to 5·4. The central portion of a fragment weighing about 12 grms. was taken for analysis. (See Table, next column).

A sample of alluvial tin ore from Cooglegong in the Geological Survey collection (No. 2026) was examined by Prof. Stanley's method. Thirty grms. yielded 28·3 grms. of cassiterite and a residue of 31 small fragments, three of

Euxenite, Cooglegong.

	Per cent.
Tantalum pentoxide	21·92
Niobium pentoxide	5·53
Titanium dioxide	29·95
Tin dioxide	nil
Thoria	1·76
Yttria	15·76
Erbia	9·27
Ceria	1·82
Lanthana and didymia	1·73
Lime	1·02
Iron protoxide	trace
Manganese protoxide	0·34
Magnesia	0·35
Uranium trioxide	6·69
Alumina	0·76
Ignition loss	2·82
	99·72

Sp. gr. 5·37.

which were quartz, three magnetite, and one monazite. The remaining 24 appeared to include both euxenite and fergusonite.

A parcel of alluvial monazite concentrates from Cooglegong contained small proportions of cassiterite, euxenite, columbite, and probably fergusonite.

Another sample of alluvial tin ore from the Shaw Tinfield near Cooglegong was also examined. It was somewhat fine grained, 70 per cent passing a 10-mesh sieve. Twenty-five grms. of the coarser particles were tested, and yielded 93 per cent cassiterite. Most of the balance was monazite, but a few small crystals of tantalite were present.

Wodgina.—In my previous paper mention was made of the occurrence of microlite in this district, and as this mineral had not previously been recorded in Australia an incomplete analysis of it was submitted to you. The analysis has since been completed, the final results being :—

Microlite, Wodgina.

Tantalum pentoxide	73·54
Niobium pentoxide	3·62
Tin dioxide	0·90
Lime	13·46
Magnesia	0·42
Iron protoxide	3·64
Manganese protoxide	0·60
Potash	0·20
Soda	1·66
Ignition loss	1·28
	99·32
Sp. gr.	5·422

No traces of ceria or yttria were detected in it.

Ixiolite (?), Wodgina.

	Per cent.	Molecules.
Tantalum pentoxide	70·49	15·9
Niobium pentoxide	7·63	2·8
Tin dioxide	8·92	5·9
Manganese protoxide	10·87	15·3
Iron protoxide	1·34	1·8
Lime	0·42	0·7
Magnesia	0·37	0·9
Ignition loss	0·18	—
	100·22	
Sp. gr.	7·36	

Another interesting mineral has recently been received from the Wodgina district. It occurs in a very fresh state in a matrix of granular albite, the latter with a little quartz and muscovite forming about 72 per cent of the ore. The remaining 28 per cent consists of a tantalate with a somewhat resinous lustre, and varying in colour from pale cinnamon-brown to dark brown. It occurs in indistinct crystalline aggregates, the system of which has not been determined. In thin slices it is sub-transparent, and apparently homogeneous except for gradual slight variations in the depth of colour, which apparently deepens under alteration along cleavages, &c. Carefully selected material was analysed with the results given above.

If the tin is present in combination this yields a formula $3MnO.3Ta_2O_5.SnO_2$. In the large proportion of tin oxide and in the light brown colour of the powder it resembles ixiolite of Nordenskiold (Kassiterotantal of Hausmann), until however, its crystallographic system has been determined, and its apparent uniformity in tin contents confirmed, its exact species must remain in doubt. The typical mangano-tantalite of Wodgina differs from it in several respects, viz. :—

1. It contains far less tin oxide (0·5 per cent as against 8·9).
2. It is not quite so hard (6·5 as against 7·0).
3. It is quite opaque even in very fine powder.
4. Its colour is black and streak brownish black.
5. Its lustre is very different.

It resembles, on the other hand, this mineral somewhat closely in—

1. Specific gravity (7·4 and 7·1).
2. Ratio of basic protoxides to acidic pentoxides being one to one.
3. Chief base being manganese, chief acid tantalic.
4. Absence of rare earths from both.

Greenbushes.—Up to the time of the writing of my previous paper no traces of crystalline form had been observed on any of the Greenbushes tantalite. I have since seen a water-worn fragment of 25 grms. in weight which exhibits a radiated structure similar to that seen in some of the Moolyella ore.

A number of stream tin ores from Greenbushes have been examined for tantalite and stibio-tantalite with negative results. It would appear as if these minerals were confined to a small portion only of the field. Tantalum has, however, been detected in clean cassiterite from this field. A clean crystal from a lode on the South Cornwall Mine was found to yield the results given below, whilst a rolled pebble from North Greenbushes yielded 1·15 per cent Ta_2O_5.

Cassiterite, Greenbushes.

	Per cent.
Tin dioxide	97·63
Tantalum pentoxide	1·76
Iron oxide, &c.	0·61
	100·00

Bellinger.—This is a new locality for tantalates, situated close to the South Coast. The rock formation is granite traversed by veins of pegmatite, one of which, twelve miles west of Point Malcolm, gave promise of yielding muscovite of commercial quality. A mineral lease, 112H, was taken up on this vein during 1907 in order to open up the mica, and in the course of operations small quantities of a black mineral were met with, which was thought to be tin ore. Examination proved it to be tantalate and niobate of iron and manganese varying from ferro-tantalite to mangano-columbite in composition. The specific gravities recorded were 5·59, 6·60, 7·10, 7·60, indicating percentages of tantalic oxide from 15 up to 75. Most of the mineral was in irregular broken fragments, but a few imperfect tabular crystals were noticed in which the faces "*a*" and "*b*" were prominently developed, whilst traces of "*u*" were also seen.

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,*

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, &c.

By PERCY H WALKER.

(Continued from p. 206).

Phenolic Disinfectant.

The phenolic soap mixtures can generally be identified as they form an emulsion with water. They consist of phenolic soaps and hydrocarbon oils and are quite variable in composition. The following scheme for analysis is only a slight modification of that given by Allen ("Commercial Organic Analysis," 3rd edition, ii., [2], 262). The only important modification consists in the recovery of light hydrocarbons, which by Allen's process would be lost.

1. *Volatile Hydrocarbons.*—Mix the sample thoroughly, weigh a portion of somewhat more than 100 grms. in an Erlenmeyer flask with a funnel. Pour about 100 grms. into a distilling flask of 150 to 200 cc. capacity, using the funnel to prevent the disinfectant from getting on the neck of the flask, weigh back the Erlenmeyer flask and the funnel, and get the exact weight by difference. The delivery tube of the distilling flask should be bent so that it can connect with a small vertical condenser; all connections are of cork. Heat the flask in a paraffin bath, slowly and carefully, not exceeding 130° C., for one and one-half hours, or until the substance becomes solid or ceases to give off volatile matter. The receiver is a small separatory funnel with a short tube, the tube of the condenser being connected with it by a cork having a groove cut into it for the free passage of air. The funnel is weighed empty, and again with the total volatile liquid; then the water is drawn off and the remaining liquid weighed as volatile hydrocarbon.

2. *Pyridine.*—Dissolve the residue in the distilling flask in water, it is usually necessary to add 60 cc. of water; heat slowly to avoid foaming and leave the flask in the steam-bath for about an hour. Wash the soapy solution into a 500 cc. separatory funnel, add dilute sulphuric acid (1 : 3) until the liqiud is distinctly acid to litmus, cool, shake with ether, drain off the acid layer and shake it twice with additional portions of ether, wash the ether twice with water, unite the acid water solutions, transfer to a large round-bottomed flask, and render distinctly alkaline with sodium hydroxide, but avoid a great excess of alkali, as it will cause foaming. Use a spray trap and a large condenser. In all distillations tie the stopper in the flasks and condensers, as they are liable to be blown out, and distil in a current of steam until all of the pyridine has passed over. This is usually a tedious operation, but in most cases the pyridine can be driven over in the first 600 or 700 cc. To ascertain whether all of the pyridine has come over, mix 10 cc. of the distillate with 10 cc. of a solution of one drop of half-normal sulphuric acid in 50 cc. of water coloured with methyl-orange. The 10 cc. of distillate should not change the colour of the solution. Transfer the distillate to a 1000 cc. graduated flask, add an excess of half-normal sulphuric acid, fill to the mark, mix, and titrate aliquots back with fifth-normal sodium hydroxide using methyl-orange. From the amount of half-normal sulphuric acid neutralised, calculate the percentage of pyridine (1 cc. of half-normal sulphuric acid corresponds to 0·0395 grain of pyridine).

3. *Heavy Hydrocarbons.*—The ethereal layer above the acid solution in which the pyridine is, contains hydrocarbons, phenols, and fatty and resin acids. Add a 25 per cent solution of sodium hydroxide in amount sufficient to combine with all the fatty and resin acids and phenols, shake, add water to dissolve the soaps, shake again and allow to settle. It will frequently be observed that there are not two layers, but three, and care must be taken to distinguish between the dark ethereal layer and the intermediate dark alkaline layer below it. Draw off the liquid underneath the ether, shake out twice again with ether, wash all ether portions three times with water, unite the ether solutions in a weighed Erlenmeyer flask, distil off the ether, dry for three-quarters of an hour on a steam-bath, wipe out the moisture from the neck of the flask, and weigh as heavy hydrocarbons. Concordant results cannot be obtained by drying to constant weight, hence it is always much better to leave the Erlenmeyer flask on the steam-bath exactly three-quarters of an hour after distilling off the ether.

4. *Phenols.*—Heat the alkaline liquid separated from the heavy hydrocarbons on the steam-bath to drive off the ether, transfer it to a round-bottomed flask, make distinctly acid with sulphuric acid (1 : 3) and distil in a current of steam until no more oily drops pass over (do not use a spray trap); to the distillate add an excess of sodium hydroxide, evaporate to about 20 cc., transfer to a narrow graduated stoppered cylinder, acidify with sulphuric acid (1 : 3) keeping it cool, mix, allow to settle over night, and measure the layer of phenol. The volume in cubic centimetres multiplied by 1·05 gives the number of grms. of phenols.

5. *Fatty and Resin Acids.*—Cool the residue in a distilling flask, extract with ether, distil off the ether, dry on a steam-bath three-quarters of an hour, cool, and weigh as fatty and resin acids.

6. *Other Tests.*—Ash a 10 grm. portion of the disinfectant and determine the alkalinity of the ash, and whether the alkali is soda or potash. In determining the relative values of disinfectants of this class, the sample should be submitted to a bacteriological test. In the absence of such a test the substance may be graded by the sum of the percentage of phenols and pyridine. This is, of course, only a general approximation, as the hydrocarbons and soaps doubtless have some germicidal action.

Pipe Covering and Cement.

1. *Sampling.*—The insulating covering for steam pipes is generally made of a hydrated basic carbonate of magnesium and serpentine asbestos. Such material is difficult to sample, but by cutting out pieces of about 1 grm. weight from twelve or more different places on the section of pipe covering, grinding in a mortar and thoroughly mixing, a satisfactory sample can generally be obtained. Preserve this sample in a tightly stoppered bottle. The cement for pipe covering is of the same composition as the cover itself and is examined in the same way, but it is much easier to sample.

2. *Moisture* (*Loss at* 105° C.).—Dry 1 grm. of the prepared sample for two hours at 105° C., weigh, and calculate loss in weight as moisture.

3. *Loss on Ignition.*—Ignite sample used for the moisture determination to constant weight. It is necessary to stir the material several times to insure heating all parts of the sample.

4. *Asbestos.*—Treat 5 grms. with 100 cc. of 6 per cent acetic acid, heating on the steam-bath to hasten solution. Filter on a Gooch crucible, wash, dry at 120° to 130° C., and weigh. This result is considered to represent asbestos. Then ignite to determine the water in the asbestos (about 14 per cent generally), which is deducted from the total, as it has already been included in the "Loss on Ignition." By this method all matter insoluble in acetic acid is assumed to be asbestos. If the presence of other insoluble material is suspected, filter on paper and examine the residue with the microscope or make an analysis of it. This, however, is seldom necessary. Serpentine asbestos is slightly soluble in acetic acid, but this error may be neglected.

5. *Alumina and Iron Oxide.*—Add ammonium chloride and ammonium hydroxide to the filtrate from the asbestos, filter, dissolve precipitate in hydrochloric acid, re-precipitate with ammonium hydroxide, filter, wash, ignite, and weigh as alumina and iron oxide.

6. *Magnesia.*—Unite the filtrates from the alumina and

* *Bulletin* No. 109, Revised, U.S. Department of Agriculture, Bureau of Chemistry.

iron oxide and make up to 500 cc. On 25 cc. of this solution determine magnesia in the ordinary manner. If the absence of all other metals has been proved the magnesium can be rapidly determined by adding sulphuric acid, evaporating to dryness, carefully heating to drive off ammonia salts and excess of sulphuric acid, and weighing as magnesium sulphate. Report the magnesium as magnesia (MgO) and calculate the equivalent of magnesium carbonate ($MgCO_3$), and also of hydrated basic magnesium carbonate $(MgCO_3)_4Mg(OH)_2.5H_2O$. The last is not a definite compound, the formula being only an approximation, but it approaches in composition the magnesium compound used in manufacturing these articles.

Rubber.

1. *Preparation of Sample.*—No general rule can be laid down for sampling all kinds of rubber goods, but pieces should be taken from as many parts of the article to be analysed as possible, and shredded by passing first through a meat chopper and then through a coffee mill. Hard rubber is best subdivided by rasping.

2. *Ash.*—Determine ash on a 1 or 2 grm. sample in a porcelain crucible, distilling off as much of the material as possible at the lowest possible temperature and completing the ashing at a very low red-heat. To completely burn out all the carbon it will be necessary to break up the ash. In case the only mineral fillers are silica or barium sulphate, the percentage of ash will give a fairly good estimate of the amount of mineral filler used; but with lead and zinc compounds there will always be more or less loss metal and with carbonates there will also be loss. A qualitative analysis should be made of the ash.

3. *Acetone Extract.*—Extract from 1 to 2 grms. of the sample with acetone, using an extractor having no rubber or cork connections and one in which the hot vapours pass around the extraction tube so that the solvent in contact with the rubber is near its boiling-point. With such an apparatus a five-hour extraction is usually sufficient. Evaporate the solvent and weigh the extract. As a check the extracted rubber may be dried in a current of hydrogen or coal-gas at 100° C., and weighed; but it is better to determine the extract by direct weighing. The acetone extract contains the free sulphur in the rubber, the resins, and the fatty and mineral oils.

4. *Free Sulphur.*—Determine the free sulphur by adding about 25 cc. of fuming nitric acid to the acetone extract, heating on the steam-bath over night, boiling to expel nitrous fumes, diluting to about 500 cc., and determining sulphur in the ordinary way as barium sulphate. Deduct the free sulphur from the total acetone extract and report "sulphur-free acetone extract."

5. *Alcoholic Potash Extract* (*Fatty Substitutes*).—Transfer the residue from the acetone extract from the extraction tube or cartridge to a small beaker, add 20 cc. of approximately normal alcoholic potash, and heat on the steam-bath for thirty minutes. Dilute with 20 cc. of water, filter through the extraction tube (first decanting off the clear supernatant liquid) into a 100 cc. flask having a rather narrow neck, and wash with water. Add an excess of sulphuric acid to the liquid in the flask, heat for twenty minutes on the steam-bath, add water to bring the liquid up into the neck of the flask, and see if any fatty acid separates. If fatty acid is found, transfer the liquid to a separatory funnel, shake out with ether, evaporate the ether, and weigh the residue. This weight divided by 0·97 gives the weight of the alcoholic potash extract (fatty substitutes).

6. *Chloroform Extract* (*Bitumens*).—Wash the residue from the alcoholic potash extract with alcohol and ether, dry in a current of hydrogen or coal-gas, extract for three hours with chloroform, evaporate the chloroform, and weigh the extract. A very small amount of chloroform extract is always obtained even when bitumens are not present, but this is generally not over 1 per cent.

7. *Total Sulphur* (*other than as Barium Sulphate*) (U.S. Dept. Agr., Bureau of Chemistry, *Bull.* 107, Revised, p. 23).—To 1 grm. of the sample in a 100 cc. nickel crucible, add about 2 cc. of water and about 5 grms. of anhydrous sodium carbonate. Mix thoroughly, using a nickel or platinum rod. Add sodium peroxide in about 0·5 grm. portions, mixing thoroughly after each addition. Continue adding the peroxide until the mixture becomes granular and nearly dry, using about 5 or 6 grms. in all. Heat the crucible with a very low alcohol or gasoline gas flame until the contents are fused, stirring all the time and carefully avoiding any overheating. (If the material ignites, the determination is ruined). Allow to cool somewhat and cover the hardened mass with a layer of peroxide to a depth of about 0·5 cm. Heat carefully to complete the fusion and keep the material fused for ten minutes. Cool somewhat, place the crucible in a casserole, and carefully add water. After violent action has ceased, remove the crucible, washing it out with water, make slightly acid with hydrochloric acid, and boil to make sure that any barium sulphate, which may have been used as a filler and was partially decomposed by the fusion, is precipitated. Filter and determine sulphur in the filtrate by precipitation with barium chloride in the usual manner. This method gives the total sulphur except that present as barium sulphate, and in case no mineral matter other than barium sulphate is present will contain no sulphur from the mineral matter. If the rubber contains sulphur other than as barium sulphate in the mineral matter, this will be included in the total sulphur.

8. *Fillers.*—As a rule the ash may be considered as fillers, but if carbon or hydrated or carbonated mineral matter has been used the ash will be less than the fillers and consequently the gum reported by difference will be too high; on the other hand, the free and combined sulphur is more or less fixed by the amount of mineral matter. An accurate method for determining fillers is much needed; but all methods proposed fail on certain kinds of rubber goods, and frequently the ash determination must be used. For most samples, except hard rubber, the following method is very satisfactory:—Extract a fresh portion of rubber with acetone; transfer 1 grm. of the extracted residue to a weighed beaker of 200 cc. capacity; add 50 cc. of camphor oil, and heat on the steam-bath until the rubber is dissolved (this usually takes about two days). When the rubber is all dissolved (as indicated by the appearance of the insoluble matter), filter through a counterpoised paper. (If the paper proves unsatisfactory use a Gooch crucible with a thick layer of asbestos). Dilute the filtrate with benzol and whirl in a centrifuge. In this way very finely divided mineral matter, which may pass through the filter, can frequently be determined. Wash the paper and beaker containing the mineral matter with hot benzol, gasoline, ether, and alcohol; then wash again with ether, dry at 105° C., and weigh.

9. *Gum.*—Add together the sulphur-free acetone extract, the alcoholic potash extract, the chloroform extract, the total sulphur, and the fillers; subtract the sum from 100 to obtain the percentage of gum present. (For further information on this subject consult the standard works on the subject, such as Weber on the "Chemistry of India Rubber," Allen's "Commercial Organic Analysis," and Lunge, "Chemisch-technische Untersuchungsmethoden").

(To be continued).

Oxy-diacetyl.—Otto Diels and Milan Farkas.—Oxy-diacetyl, $CH_2(OH).CO.CO.CH_3$, represents an unknown type of compound, and should possess the properties both of a carbohydrate and an α-diketone. The authors have found that from the monoxime of diacetyl a monobrom derivative can readily be obtained: — $CH_3.CO.C(:N.OH).CH_3 \rightarrow CH_2Br.CO.C(:N.OH).CH_3$. The latter reacts with potassium acetate to give an acetyl compound, $CH_2(O.CO.CH_3).CO.C(:N.OH).CH_3$, which on saponification gives the oxime of oxy-diacetyl, $CH_2(OH).CO.C(:N.OH)CH_3$. The preparation of oxy-diacetyl from this monoxime has not yet been effected.—*Berichte*, xliii., No. 11.

THE CITRATE-SOLUBILITY OF PHOSPHORIC OXIDE IN BASIC SLAG.*

By E. V. FLACK, F.C.S.

At a meeting of this Society held on November 26th, 1909, Dr. R. Marloth read a paper on the subject of the solubility of the phosphoric oxide contained in basic slag in citric acid and citrate solutions. He pointed out that the different methods in use for the determination of citrate-soluble phosphoric oxide gave varying results and suggested that a uniform method be adopted in South African laboratories.

Since the above paper was read I have performed a number of determinations of citrate-soluble phosphoric oxide in basic slag, both with Petermann's solution and a 2 per cent citric acid solution as solvent.

Before giving any analytical figures I shall state in detail the solutions used by me and the methods employed for the actual analysis.

Solutions Employed.

1. *Petermann's Solution.*—250 grms. of crystallised citric acid are dissolved in half a litre of hot water, diluted with 550 cc. of water, 276 cc. of 24 per cent ammonia solution added, and the solution finally exactly neutralised by adding 50 per cent citric acid solution little by little, using litmus-paper as indicator. The solution when ready for use should have a specific gravity of 1·09.

2. *Citric Acid Solution.*—20 grms. of crystallised citric acid dissolved in 1 litre of distilled water.

3. *Citrate Solution.*—150 grms. of citric acid are dissolved in water treated with 500 cc. of 24 per cent ammonia solution and the mixture made up to 1500 cc.

4. *Magnesia Mixture.*—55 grms. of magnesium chloride, 105 grms. of ammonium chloride, 350 cc. of 24 per cent ammonia solution, and 650 cc. of distilled water.

5. *Ammonia Solution.*—24 per cent ammonia solution. Strong 0·880 ammonia solution.

The methods employed for the analysis were as follows:—

A. *Total Phosphoric Oxide in Slags.*

For the estimation of the total phosphoric oxide 10 grms. of the substance are moistened in a porcelain dish with a few drops of water, about 5 cc. of dilute sulphuric acid (one to one) are added, and, as soon as the mass has hardened, 50 cc. of concentrated sulphuric acid are poured on, and the mixture is gently broken up with a glass rod until the whole mass has become uniform.

The mixture is now well heated on a sand-bath for half-an-hour.

It is then allowed to cool and washed over into a half litre flask, when cold filled up to mark, filtered, and 50 cc. of the filtrate taken for the determination, and treated as under Petermann's, except that 100 cc. of the citrate solution are employed.

The difference between the total phosphoric oxide and the insoluble phosphoric oxide in extraction by Petermann's solution gives the amount of citrate-soluble phosphoric oxide.

It is well known that in England and on the Continent of Europe the soluble phosphoric oxide in basic slag is expressed in terms of that soluble in a solution of 2 per cent citric acid.

B. *Extraction by Means of Petermann's Citrate Solution.*

2 grms. of the substance are digested with 100 cc. of Petermann's solution of specific gravity 1·09 for half-an-hour at 50° C. in a beaker. The insoluble matter is then filtered off by the aid of the filter-pump, and the residue is washed with a mixture of equal parts of water and Petermann's solution, until all dissolved phosphoric oxide is washed out of the filter; three or four washings usually suffice to accomplish this.

The residue on the filter is dried, ignited at a low temperature, and dissolved in a mixture of 2 cc. of nitric acid and 20 cc. of sulphuric acid in a 200 cc. flask, when cold diluted up to the mark, filtered, and 100 cc. of the filtrate, equivalent to 1 grm. of original substance, taken for the determination. The acid in the filtrate is nearly neutralised, 50 cc. of the citrate solution added, then 25 cc. of magnesia mixture, and finally 20 cc. of 24 per cent ammonia solution.

After standing forty-eight hours the precipitate is separated by filtration, ignited, and weighed in the usual way.

Until recently the above was the method of determination adopted in the Cape Government laboratories.

C. *Extraction by Means of 2 Per Cent Citric Acid Solution.*

For the following method I am indebted to F. Plant, Esq., who very kindly obtained same from a large European firm in the fertiliser trade.

a. Rendering the Silica Insoluble.—5 grms. of the substance are weighed out and placed in a litre flask, and 500 cc. of a 2 per cent citric acid solution poured in, and the flask is closed with a rubber stopper and gently and continuously agitated for half-an-hour at the ordinary temperature.

The solution is then immediately filtered and the phosphoric oxide is determined in an aliquot part of it.

Various methods of determining the phosphoric oxide in this solution are in vogue on the Continent, but some of these are liable to be seriously affected by the presence of dissolved silica.

Using 200 cc. of the filtrate (equivalent to 2 grms. of the substance) the silica is removed by evaporation to dryness with strong hydrochloric acid, and 16 grms. of citric acid are placed in the dish or beaker, and about 30 cc. of water and from 10 to 15 cc. of strong hydrochloric acid are added. After digestion on a water-bath until the citric acid is dissolved the contents of the beaker are stirred thoroughly and filtered, and the insoluble silica washed first with a little dilute hydrochloric acid, then with very small quantities of boiling water until nearly free from acidity, the phosphoric oxide being determined in the filtrate as follows:—The filtrate should not measure more than 150 cc. Magnesia mixture is added (at least twice as much as is necessary to precipitate the phosphoric oxide—10 cc. of magnesia mixture will precipitate 0·168 grm. of P_2O_5), and then a considerable excess of strongest ammonia solution. The total bulk should then measure about 220 cc., about one-fifth to one-sixth of the solution should be 0·880 ammonia. Then stir for at least fifteen minutes with a rapid mechanical stirrer; or if the stirring is by hand, for half-an-hour. After this allow to rest, with occasional stirring, for at least half-an-hour. Then filter and wash the precipitate with dilute ammonia solution; ignite and weigh as $Mg_2P_2O_7$.

When using 2 grms., the weight of the precipitate multiplied by 32 gives accurately the percentage of phosphoric oxide, provided that the quantities above-mentioned are taken for analysis.

b. Without Rendering the Silica Insoluble.—50 cc. of the filtrate (equivalent to ½ grm.) of the original substance are placed in an Erlenmeyer flask, 50 cc. of the citrate solution are added from a burette; should, however, a turbidity take place an additional quantity to 25 cc. of the citrate solution is added. The addition of the magnesia mixture must follow as quickly as possible after the addition of the citrate solution to avoid a separation of crystalline calcium phosphate. On the addition of the citrate solution there is always a rise of temperature. Inasmuch as the precipitation of the phosphoric oxide with magnesia must take place in the cold, the liquid must be cooled as quickly as possible.

The following analytical results have been arrived at by the various methods. For sake of comparison I have given where possible the figures obtained in Europe by manufacturers' chemists.

* Read at a Meeting of the Cape Chemical Society held on August 26th, 1910.

No. of sample.	Method B.	Method C (*a*).	Method C (*b*).	European guarantees.
1.	11·42	—	15·68	15·46
2.	12·13	—	17·53	16·37
3.	12·65	—	15·10	15·07
4.	9·03	—	13·75	13·15
5.	10·58	—	15·61	14·94
6.	12·10	—	16·27	14·59
7.	—	15·43	15·96	14·78
8.	—	14·86	15·38	14·70
9.	—	12·13	12·82	—
10.	—	12·05	12·43	—
11.	—	14·84	15·38	14·90
12.	—	13·51	13·61	14·09

It may be noted that the results obtained by method C(*b*) are roughly speaking half of 1 per cent higher than those obtained by method C (*a*).

It may be of interest to place on record the amount of silica dissolved during the half hour shaking with the 2 per cent citric acid solution from the samples Nos. 7 to 12.

No. of sample.	Per cent of silica.
7.	8·08
8.	7·56
9.	10·26
10.	10·41
11.	8·34
12.	9·44

The residue of silica was completely volatilised by treatment with hydrofluoric acid, and was therefore pure silica, with the exception of samples 7 and 8, which contained unweighable traces of phosphate.

All the above determinations were made on the product obtained by sifting the slag through a standard sieve of 10,000 meshes to the square inch (*i.e.*, $\frac{1}{4}$ mm. linear).

On consideration of the above results it will be seen that the differences between the Petermann's *citrate*-soluble and the *citric acid*-soluble phosphoric oxide are enormous, and that the South African laboratories (especially now that there is a Fertiliser Act in force) will have to employ the method C (*a*) as official in the case of basic slags, if they desire to have the results comparable with those obtained by English and European chemists.

In conclusion, I wish to express my thanks to Mr. D. Millin, B.A., for his valuable help in the work.

NOTICES OF BOOKS.

Forty-sixth Annual Report on Alkali, &c., Works. By the Chief Inspector. London: Wyman and Sons, Ltd. 1910.

This annual report contains a memorandum on the analysis of ammoniacal liquors obtained in the manufacture of coalite, in which the presence of organic matter interferes with ordinary methods of estimation. The memorandum gives details of the processes now adopted for the determination of free and fixed ammonia, carbon dioxide, chloride, sulphur, ferrocyanide, and hydrocyanic acid, the last two methods being those worked out by Herr Walther Feld. A report is also given of investigations of coal carbonising, and the interaction of methane and ammonia in presence of carbon.

A Treatise on Electro-metallurgy. By Walter G. McMillan, F.I.C., M.Inst.M.M. Revised by W. R. Cooper, M.A., B.Sc., A.I.C. Third Edition. London: Charles Griffin and Co., Ltd. 1910.

This comprehensive text-book of electro-metallurgy treats both the theory and practice of the application of electrolysis to the plating, smelting, refining, &c., of metals in sufficient detail for the purposes of both the student and the practical man. Each of the important metals is given a chapter, and the recovery of certain of them from their solutions, the power required for electrolytic work and its cost are all discussed with completeness and lucidity. A glossary of common substances employed in electro-metallurgy is added. In the third edition the section on the construction and use of the dynamo is omitted, the reviser believing that it was impossible to treat it adequately in the space which could be spared for it, and a new chapter has been added on the electric smelting and refining of iron.

MISCELLANEOUS.

Port Rates on Goods.—We are officially informed by the Port of London Authority that on and after November 1st next Port Rates will be payable in respect of all goods imported or exported into or from the Port of London from or to parts beyond the seas or coastwise. The rates will be payable at the Office of the Collector, 13 and 14, George Street, Tower Hill, E.C., between the hours of 8 a.m. and 4 p.m., Sundays and public holidays excepted. Each payment must be accompanied by a bill giving particulars of the goods in respect of which it is made. Copies of the list of Port Rates containing also information relative thereto and forms of bills can be obtained at 109, Leadenhall Street on and after Monday, October 24th. Deposit accounts, which must be entirely independent of any other Deposit accounts for rates or charges, may be opened for the payment of Port Rates, and this may be done at the Collector's Office on and after Wednesday, October 26th.

NOTES AND QUERIES.

Heats of Formation.—Can any reader furnish information respecting the methods by which the heats of formation of hydrochloric acid, hydriodic acid, and ammonia have been accurately determined? This has proved of difficulty to several of my student friends, as well as to myself.—R. C. Hawkins.

MEETINGS FOR THE WEEK.

Wednesday, Nov. 2nd.—Society of Public Analysts, 8. "Estimation of Lactose in the presence of the commonly occurring Sugars," by J. L. Baker and H. F. E. Hulton. "Colorimetric Estimation of Hydrogen Cyanide," by A. C. Chapman. "Polarimetric Estimation of Milk-sugar," by H. D. Richmond. "New Method of Estimating Phosphoric Acid," by G. F. W. Martin.

Thursday, 3rd.—Royal Society. "Origin of the Hydrochloric Acid in the Gastric Tubules," by Miss M. P. Fitzgerald. "Trypanosome Diseases of Domestic Animals in Uganda—II., *Trypanosoma Bruci*; III., *Trypanosoma vivax*," by Col. Sir D. Bruce and others. "Further Results of the Experimental Treatment of Trypanosomiasis—being a Progress Report to a Committee of the Royal Society," by H. G. Plimmer, Capt. W. B. Fry, and Lieut. H. S. Ranken. "Peculiar Morphology of a Trypanosome from a Case of Sleeping Sickness and the possibility of its being a New Species," by Dr. J. W. Stephens and Dr. H. B. Fantham. "Examination of the Tissues of the Central Nervous System, with Negative Results, of a Case of Human Trypanosomiasis, which apparently had been cured for years by Atoxyl Injections," by Dr. F. W. Mott. "Remarkable Pharetronid Sponge from Christmas Island," by R. Kirkpatrick

— Chemical, 8.30. "Researches on Bleaching Powder," by R. L. Taylor. "Azomethine Azo-dyes," by A. G. Green and R. N. Sen. "Synthesis in the Epinephrine Series—Part II., The Formation and Properties of some 2:5- and 2:6-Substituted Pyrazines and their Conversion into Aminoketones and Iminodiketones," by F. Tutin. "Absorption Spectra of some Substituted Perazines and their Salts," by F. Tutin and F. W. Caton. "Studies in the Camphane Series—Part XXVIII., Stereoisomeric Hydrazones and Semicarbazones of Camphorquinone," by M. O. Forster and A. Zimmerli. "Constituents of Gelsemium," by C. W. Moore. "Some Phenolic Derivatives of β-Phenylethylamine," by G. Barger and A. J. Ewins. "Chloramine Reactions—Methylene Chloramine," by C. F. Cross and E. J. Bevan. "Preparation of Secondary Amines from Carboxylic Acids—Part I., Preparation of Heptadecylaniline, Pentadecylaniline, and Tridecylaniline," by H. R. Le Sueur.

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THE DEVELOPMENT OF THE ATOMIC THEORY.

III.—Newton's Theory and its Influence in the Eighteenth Century.

By ANDREW NORMAN MELDRUM, D.Sc.
(Carnegie Research Fellow).

i. *The Atomic Theory of Newton.*

One of the great obstacles to a right understanding of the history of science is the tendency of writers to let their attention be absorbed by one individual, who thus engrosses the credit for important ideas and discoveries, to the neglect of deserving predecessors. Besides the injustice of it, this method gives a distorted view of the progress of science. For instance, Nernst, apropos of Dalton, remarks that the atomic hypothesis "by one effort of modern science, arose like a phœnix from the ashes of the old Greek philosophy" (Nernst, "Theoretische Chemie," 5th Ed., p. 34). This sweeping statement ignores atomic speculation between the time of Lucretius and the nineteenth century. As if the atomic theory of Newton were perfectly negligible!

This paper is written in the belief that the atomic theory has gone through a process of development from the time of Leucippus up to the present. The main conclusions are (1) that Newton made a contribution to the said process, (2) that he did so under the influence of Descartes, and (3) that he was in turn himself an influence in the eighteenth century.

In the seventeenth century the atomic theory is associated with the famous names of Francis Bacon (1561-1626), René Descartes (1596—1650), Pierre Gassend (1592—1655), Robert Boyle (1627—1691), and Isaac Newton (1642—1727).

Bacon recurs to the theory again and again in his philosophical writings, as if fascinated by it. But he changed his mind on the subject, tending as time went on to become more and more distrustful of *a priori* reasoning. At one time he entertained great expectations from the study of the atoms. "I know not whether this inquiry I speak of concerning the first condition of seeds or atoms be not the most useful of all, as being the supreme rule of act and power, and the true moderator of hopes and works" ("Bacon's Works," edited by Spedding and Ellis, v., 423). This is in the "Cogitationes de Natura Rerum," which is regarded as having been composed before the year 1605. But his mature judgment, as expressed in the "Novum Organum," published in 1620, was that the atoms are an unprofitable study:—"Men cease not . . from dissecting nature till they reach the atom; things which, even if true, can do but little for the welfare of mankind" (*op. cit.*, iv., 68; "Novum Organum," i., Aphorism 66).

Robert Boyle in this country was the exponent of the atomic theory who brought it into repute. In the year 1659 he urged the "desirableness of a good intelligence between the Corpuscularian philosophers and the chemists" ("Boyle's Works," edited by Birch, 1744, i., 227), and this topic for some time afterwards he made a leading theme in his scientific writings. Within a few years of his first attempt he was able to say that he has "had the happiness to engage both divers Chymists to learn and relish the notions of the Corpuscular Philosophy, and divers eminent embracers of that to endeavour to illustrate and promote the New Philosophy by addicting themselves to the experiments and perusing the books of chemists" (*op. cit.*, ii., 501).

Boyle, while on this topic, mentions Descartes and Gassend much oftener than any other philosophers. Descartes believed in the existence of atoms, and at the same time he denied that a void could exist. A subtle fluid occupied the space between the atoms, and even permeated them. Hence the vortex motion which had been set up in the fluid could not but communicate itself to the atoms. An admirable description of the atmosphere, according to the Cartesian theory, is to be found in Boyle's "New Experiments, Physico-mechanical, touching the Spring of the Air." "The restless agitation of that celestial matter, wherein these particles [of air] swim, so whirls them round, that each corpuscle endeavours to beat off all others from coming within the little sphere requisite to its motion about its own centre . . . their elastical power is made to depend . . . upon the vehement agitation . . ., which they receive from the fluid ether that swiftly flows between them" (*op. cit.*, i., 8). It is remarkably difficult to find in Descartes so good a description of his theory as this. (See, however, "Œuvres," edited by Cousin, v., 159—162, 169—170).

Descartes's denial that a vacuum could exist, it is plain from this, is not to be taken in its cruder sense. He never meant and never said that space is full of matter of the ponderable kind. (Clerk-Maxwell might well have emphasised this in his comments on the "Error of Descartes," "Matter and Motion," Article XVI.). He meant, surely, that in the absence of ponderable matter space is occupied by ether, "the celestial matter." In short, that "we have no means of producing an ether-vacuum."

A more conventional theory is due to the revival by Gassend of the Epicurean philosophy.* His interest in this was such that he devoted himself for some twenty years to the study of Epicurus and Lucretius the Epicurean. Gassend sought to connect the atomic theory with both physical and ethical problems, for those were the days when natural and moral philosophy were studied by the same persons. He brought out three books on the subject between the years 1647 and 1649, one of which, the "Syntagma Philosophiæ Epicuri," was well known to Boyle.

Boyle learnt of the book through his friend Samuel Hartlib. As Hartlib wrote to him in a letter dated London, May 9th, 1648:—"Your worthy friend and mine, Mr. Gassend, is reasonable well, and hath printed a book of the life and manners of Epicurus since your going from hence. He hath now in the press at Lyons the philosophy of Epicurus, in which I believe we shall have much of his own philosophy, which doubtless will be an excellent work" ("Boyle's Works," edited by Birch, 1744, v., 257). Boyle in one of his essays advises Pyrophilus to read the "learned Gassendus, his Little Syntagma of Epicurus's Philosophy, and that most ingenious gentleman Mons. Descartes, his Principles of Philosophy" (*op. cit.*, i., 194). There was then, as there is still, a tendency to regard Descartes and Gassend as opponents of one another on the principles of the atomic theory. Boyle mentions some "learned men as more favouring the Epicurean, and others (though but a few) being more inclinable to the Cartesian opinions." However, he did not see any necessity to ally himself with one party or the other. "Notwithstanding those things, wherein the atomists and the Cartesians differed, they might be thought to agree in the main, and their hypotheses might, by a person of a reconciling disposition, be looked on . . . as one philosophy" (*op. cit.*, i., 227—228).

Science has often gained immensely by a wise limitation of the problem to be solved. Descartes's theory that space is pervaded by an ethereal fluid, and that ordinary matter consists of atoms swimming in the ether, is formally complete, and has to be adopted sooner or later. Yet Gassend's theory, which is incomplete, since it ignores the ether and concentrates attention on the atoms, proved more helpful to science in the first instance. Newton was

* The best account of Gassend known to me is that given by Dr. John Masson in his "Lucretius, Epicurean and Poet," vol. II., Chapter I.

more inclined to Gassend's way of thinking than to Descartes's. In the "Principia" he would not consider the mechanism of gravitation, and in the course of his atomic speculations he almost leaves out of account the means by which chemical attraction arises. Nevertheless, Newton was influenced by Descartes.

The Cartesian natural philosophy was predominant throughout Europe for the most part of the seventeenth century, and in the eighteenth the Newtonian philosophy, as expounded in the "Principia," took its place. The two philosophies being opposed to one another, no one apparently has reflected how much Newton may have been indebted to Descartes. The mere fact that Cartesianism was dominant during the seventeenth century means that Newton must have made himself master of that system of nature. Presumably then, whatever was sound in Descartes, he retained and assimilated. Boyle and Hooke had studied Descartes, and Newton studied all three. He acknowledges his indebtedness to others in a letter to Hooke, dated Feb. 5th, 1675/6, on the subject of Light:—"You defer too much to my ability in searching into this subject. What Descartes did was a good step. You have added much several ways, and especially in considering the colours of thin plates. If I have seen further, it is by standing on the shoulders of Giants" (Brewster's "Life of Newton," i., 142).

Newton, in his speculations on the disintegration of atoms, in Query 31 of the "Opticks," had no unusual physical phenomenon in view at the time. He was simply improving on Descartes, whose theory on that subject seems crude enough ("Œuvres," edited by Cousin, iv., 266—268*). In contrast to these speculations Newton took up a problem which was a perfectly concrete one.

Boyle's law, that the volume of a given quantity of air is inversely proportional to the pressure, had been made known in the year 1662. Newton's theory of gravitation was based on the assumption that every particle of matter attracts every other particle. In explaining Boyle's law he made the very different assumption that air is composed of particles which repel one another.

This conception of the atmosphere as being composed of "particles mutually repulsive" was in all probability derived from Descartes. Boyle, in the passage already quoted, where he explains the Cartesian theory, says that in the air, "Each corpuscle endeavours to beat off all others from coming within the little sphere requisite to its motion about its own centre."

Newton proved that the air must obey Boyle's law, if the force of repulsion between its particles were inversely proportional to the distance between them. He does not mention Boyle, or the air, but puts the matter in the most abstract way by advancing the following proposition:—"If the density of a fluid, which is made up of mutually repulsive particles, is proportional to the pressure, the forces between the particles are reciprocally proportional to the distance between their centres and *vice versa*, mutually repulsive particles, the forces between which are reciprocally proportional to the distances between their centres will make up an elastic fluid, the density of which is proportional to the pressure" ("Principia," Book 2, Prop. 23).

Newton does not draw any inference as to the nature of the atmosphere. "All these things are to be understood of particles whose centrifugal forces terminate in those particles that are next them, or are diffused not much further. We have an example of this in magnetical bodies. . . . Whether elastic fluids do really consist of particles repelling each other is a physical question. We have here demonstrated mathematically the property of fluids consisting of particles of this kind, that hence philosophers may take occasion to discuss that question."

This proposition, along with its proof in the "Principia," is the earliest instance of the mathematical treatment of the atomic theory. Svante Arrhenius declares that the "atomic theory remained in the hypothetical stage for about 2300 years, as no quantitative conclusions were drawn from it till the time of Dalton" (Arrhenius, "Theories of Chemistry," Eng. trans., p. 15). This statement entirely ignores Newton's explanation of Boyle's law in terms of atoms, as well as certain workers in the eighteenth century who were under Newton's influence.

ii. *Newton's Influence in the Eighteenth Century.*

In the last quarter of the eighteenth century a very remarkable attempt at a chemical atomic theory was made by two Irishmen, by name Bryan Higgins and William Higgins. The object of the second and concluding part of this paper is to show that the theory advanced by Bryan Higgins, and amplified by William Higgins, can be understood only when regarded as springing from Newton's theory under the peculiar conditions of the time. These conditions were:—(1) The knowledge, due to Priestley, of different kinds of gases, and (2) the new light which Lavoisier threw on chemical composition, consequent on Priestley's discovery of oxygen.

The senior of the two men,* Bryan Higgins (1737—1820), was self-taught in chemistry, and his career proves him to have been the best all-round man among the English-speaking chemists of his day. His "Experiments and Observations concerning Acetous Acid" (1786) is a record of a very thorough investigation in the field of organic chemistry. As a technical chemist his reputation was wide. He was a pioneer in the practical teaching of chemistry, and gave instruction in the subject for some twenty-three years (1774—1797) in his School of Practical Chemistry in Greek Street, Soho, London.

His most important publication, in connection with the atomic theory, is a "Philosophical Essay concerning Light" (1776). This essay is very different from what it purports to be. It contains a fragment only—all that was ever published—of the essay on light that Higgins had designed. The major part of the book is simply an expansion and exposition of a syllabus of chemistry which he had published earlier, in 1774 or 1775, and which also is prefixed to the essay.

Higgins had gone to Newton for inspiration: the "Philosophical Essay" is full of quotations from the "Opticks." Nor need there be any wonder at Higgins making his approach to the study of light by way of chemistry, since Newton's views on chemical subjects are to be found in the "Opticks" more than in any other of his books.

The discovery of new facts always gives a stimulus to speculation. The impulse in Higgins' case came from Joseph Priestley, who showed in the year 1775 that the alkaline substance ammonia, and various acids, hydrochloric, for instance, can exist in the gaseous state. Higgins thereupon proceeded to adapt the Newtonian conception of a gas to the processes of chemistry. Gaseous particles of the same kind were "mutually repulsive," but what should happen in case acid and alkali were brought together? Higgins said that the acid particles and the alkaline attracted one another, and formed a neutral salt by combining *particle with particle*. He thought an acid and an alkali must combine with one another in one proportion only, a combination of two particles of acid and one of alkali, or of two of alkali and one of acid being precluded, because the two similar particles must repel one another.

Higgins laid great stress on this force of repulsion between particles of the same kind. On this line of thought he finds the answer to his own question:—"Why do many salts crystallise nearly neutral in a liquor containing a superabundant quantity of acid and [*sic*] of alkali?" Further, on the supposition that particles of water and of acid attract one another, and also particles of water and of alkali, he thought he could account for the water of crystal-

* I am indebted to my friend, Mr. J. R. Partington, B.Sc., for pointing out to me that Descartes was the source of Newton's ideas on the disintegration of atoms.

* For fuller information regarding Bryan Higgins and William Higgins, see *Brit. Assoc. Rep.*, Dublin Meeting, 1908, p. 668, and *New Ireland Review*, 1910, xxxii., pp. 275—286 and 350—364).

lisation found in many salts. So he explains "why much water doth combine in the crystals of most neutral salts? and why this water of crystallisation separates from the superfluous acid or alkali, and introduces little or none of either into the crystals?" (Bryan Higgins, "A Philosophical Essay concerning Light," pp. 201 – 206, 212 – 213).

In short, on the basis of Newton's theory of a gas, Bryan Higgins taught that chemical combination takes place between acid and alkali in a definite and single proportion. He went little further, if any, with these speculations. His progress must have been greatly hampered by his belief, to which he adhered till about the year 1792, in the phlogiston theory of chemistry and in the existence of seven chemical elements, namely, earth, water, air, acid, alkali, phlogiston, and light.

William Higgins (1769?—1826) was trained in chemistry by his uncle. He held various public appointments as a chemist in Ireland, and published three books, one of which is of special importance. He did not long suffer from the disadvantages of the phlogiston theory, for he was one of the first to abandon it—in 1785, he says—and was absolutely the first to write against it in the English language. His "Comparative View of the Phlogistic and Anti-phlogistic Hypotheses" (1789) is primarily a refutation of the phlogiston theory. Incidentally it shows that he had been carrying on experimental work of his own, and also that he had improved on his uncle's speculations. Out of atoms and molecules he fashioned a theory of chemical combination and of chemical dynamics as well, so that his book is remarkable as containing the first attempt at a comprehensive system of chemistry based on the atomic theory.

William Higgins regarded the atom of a gas as a hard particle surrounded by an "atmosphere of fire" (W. Higgins, "Comparative View of the Phlogistic and Anti-phlogistic Hypotheses," pp. 14, 37, 81, 133). He believed firmly that chemical combination occurs in definite proportions, and supposed that it occurs, in the first place, atom with atom. He regarded the molecule of water as formed by the linking of one atom of hydrogen with one of oxygen. "Water is composed of molicules formed by the union of a single ultimate particle of dephlogisticated air to an ultimate particle of light inflammable air . . . they are incapable of uniting to a third particle of either of their constituent particles" (*Ibid.*, p. 37). In short, the formula OH expresses his conception of the molecule of water.

William Higgins was better acquainted with the facts of chemical composition than his uncle, for he did not believe in phlogiston, and recognised oxygen as one of the elements. He was aware of a number of cases in which elements combine in more than one proportion, and in such cases continued to apply the atomic theory. He thought an element R must form oxides in the order RO, RO_2, RO_3, &c. Thus he regarded sulphurous acid virtually as SO and sulphuric acid as SO_2 (*Ibid.*, pp. 36—37). He recognised five oxides of nitrogen, and regarded them as NO, NO_2, NO_3, NO_4, and NO_5 (*Ibid.*, pp. 132—135). These ideas of chemical composition are based on the assumption that similar atoms repel one another, an assumption which is also the basis of his system of chemical dynamics. He argued that by reason of this force of repulsion the compound RO is more stable than RO_2, RO_2 than RO_3, and so on.

The line of thought taken by the Higginses afterwards proved extremely valuable. But it was not followed up at the time. William Higgins' book, which reached a second edition in 1791, was read as a contribution to the phlogiston and anti-phlogiston controversy; that was the absorbing topic in science then, and nothing else could be duly attended to.

The history of this eighteenth century movement proved a difficult problem in the succeeding century. It occupied the attention at different times of such persons as William Charles Henry, R. Angus Smith, and, in collaboration, Roscoe and Schlorlemmer. There was also a long and doubtful controversy regarding the merits of William Higgins and John Dalton, the discussion of which is left to a future paper.

Angus Smith's estimate of Bryan Higgins is a vastly different one from that advanced in this paper. His main conclusions are that Bryan Higgins' "opinions on atoms might have been held by the ancients" (R. Angus Smith, "Memoir of Dalton," p. 175); "that his theory was not clear, or he would have been led by it to decide on the necessity of fixed constitution as a result. But we obtain no results affecting chemical philosophy" (*Ibid.*, p. 173). In this paper I have shown that Bryan Higgins' theory, far from being "ancient," is a development of Newton's, and that instead of his theory being obscure and leading to confused ideas regarding chemical composition, it led to a view of the doctrine of fixed proportion, of which the fault was that it was too narrow and rigid.

This difference of opinion, great and hopeless as it may seem, admits of the simplest explanation. Smith's estimate is based upon the "Syllabus" of the year 1775, and upon certain incidental remarks on atoms which he found in the book on acetous acid. He was not acquainted with the "Philosophical Essay on Light," which assuredly is not the place where one should expect to find the chemical speculations and ideas regarding atoms, of which, nevertheless, it is full. Had Smith read this book he must have perceived the clue to the Higgins' ideas, namely, the connection with Isaac Newton. He must then have seen that Bryan Higgins was the first to explain the constant chemical composition of salts in terms of atoms, and that his theory was only too definite and rigid, for it led him to maintain that an acid and an alkali could combine in only one proportion.

W. C. Henry's estimate of William Higgins has the fatal weakness that he has quite failed to perceive what was the basis of the theory. Having given Higgins' views regarding the atomic composition of the oxides of nitrogen, he remarks:—"It is evident that Mr. Higgins was guided by no fixed and uniform principle in assigning the atomic constitution of the above compound bodies" (W. C. Henry, "Life of Dalton," p. 77). This verdict must be set aside also. No great penetration of mind is required to divine "the fixed and uniform principle" on which Higgins proceeded in assigning the atomic composition of substances. Although he does not himself mention Newton, there is no room for doubt that Newton's conception of "particles mutually repulsive" was the germ of the theory. Bryan Higgins, who was a student of Newton, made use of this conception, and he communicated it to his nephew. The indebtedness of the nephew to the uncle is as plain as the indebtedness of the uncle to Newton.

There remains now for consideration a remark made by Roscoe and Schorlemmer, that "all upholders of an atomic theory" previous to Dalton, "including even [William] Higgins, had supposed that the relative weights of the atoms of the different elements are the same" (Roscoe and Schorlemmer, "Non-metallic Elements." 1905, p. 35). This is a sweeping assertion, of which no proof has ever been offered. One can hardly believe that Newton expressed such an opinion, and it is certain that William Higgins did not. Regarding the oxidation of tin, he supposed that 100 grains of the metal may combine with $7\frac{1}{2}$ or with 15 grains of oxygen ("Comparative View," p. 275). But since he held the oxidation series of an element to be RO, RO_2, RO_3, &c., his figures for tin mean that the atom of the metal was supposed to be much heavier than one atom, or even two, of oxygen. Possibly Roscoe and Schlorlemmer's statement is based on the case of oxygen and sulphur, which Higgins held to have the same atomic weight. But this conclusion of his depends, for one thing, on the supposition that the molecule of sulphurous acid (SO_2 not H_2SO_3) is composed of one atom of each element, and for another on the experimental fact that the acid is formed by the union

of equal weights of the two elements. Higgins proved, quite correctly on his supposition, that the atomic weights of sulphur and oxygen are equal. But proof and assumption are two very different things. Surely it is one thing to prove a result in a particular case, and quite another to assume the result in general.

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A NEW THEORY OF MOLECULAR VOLUMES.

By GERVAISE LE BAS, B.Sc.

(Continued from vol. xcix., p. 206).

In previous papers open-chain and cyclic hydrocarbons have been dealt with, together with the "atomic volumes" of C and H. It is necessary to calculate the volumes of other atoms also. In many cases it will be useful to find the volumes of various substituting groups, OH, CO, CHO, COOH, because they often occur in organic compounds, and their approximate magnitude can in many cases be determined fairly accurately by a direct method. In most groups the first, and in some cases the second member also, are omitted, as they usually possess exceptionally large volumes. This is found to be the case with methane and ethane among the hydrocarbons, with formaldehyde and acetaldehyde, &c. Molecular volumes is not the only physical property in which this is the case.

Oxygen Compounds.

The Alcohols—The OH *Group. Direct Determination.*

H_2 = M.V. of C_3H_7OH − M.V. of C_3H_5OH = 81·4 − 74·2 = 7·2.

The volume of H is thus about normal, also that of C. H = 3·7, C = 14·8.

$$\left.\begin{array}{l} OH = 81{\cdot}4 - (3\times 14{\cdot}8 + 7\times 3{\cdot}7) = \\ \quad 81{\cdot}4 - 70{\cdot}3 = 11{\cdot}1 \\ OH = 74{\cdot}2 - (3\times 14{\cdot}8 + 5\times 3{\cdot}7) = \\ \quad 74{\cdot}2 - 62{\cdot}9 = 11{\cdot}3 \end{array}\right\} OH = 11{\cdot}1 = 3H.$$

The volume of OH is equal to 3H and of O′ = 7·4 = 2H. Thus, summing up the hydrogen values W—counting 4 for C—and dividing M.V. by W (a constant), the volume of H is obtained. The M.V. of O′ is again equal to the valency number of the element.

Table XIII.

Alcohol.	W.	M/V.	Δ for CH_2.	V/W.
Propyl, C_3H_7OH ..	22	81·4 S		3·70
Butyl, C_4H_9OH ..	28	101·8 S	20·4	3·64
Amyl, $C_5H_{11}OH$ ..	34	123·6 Z	21·8	3·64
Hexyl, $C_6H_{13}OH$ ..	40	146·3 Z	22·7	3·66
Heptyl, $C_7H_{15}OH$.	46	168·7 Z	22·4	3 66
Octyl, $C_8H_{17}OH$ ..	52	190·9 Z	22·2	3·67
Averages			21·9	3·66
			6×3·65	

S (Schiff). Z (Zander).

The Ethers and Ethereal Oxygen.

The volume of oxygen is abnormally large in the aliphatic ethers, or about equal to 3H = 11·1. In the phenolic ethers the oxygen = H_2 = 7·4 like hydroxyl oxygen.

Sometimes isomeric compounds possess slightly different volumes, but it is not necessary to enter into this question here. The list is also much longer, and according to the general rule the value V/W increases slightly from compound to compound, but with a preservation of the relative volumes of the atoms (*q.v.*).

The M.V. of ethidene diethyl ether $C_2H_4(OC_2H_5)_2$ is 160·2 S, and is about normal, for since W = 44 V/W = 3·64.

Table XIV.

Ether.	W.	M.V.	Δ for CH_2.	V/W.
Methyl ethyl, $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O$..	23	84·0 D	22·2	3·65
Diethyl, $(C_2H_5)_2O$ . ..	29	106·2 D		3·66
Ethyl propyl, $\left.\begin{matrix}C_2H_5\\C_3H_7\end{matrix}\right\}O$.	35	128·1 D	21·9	3·66
Ethyl butyl, $\left.\begin{matrix}C_2H_5\\C_4H_9\end{matrix}\right\}O$..	41	150·3 D	22·2	3·67
Propyl butyl, $\left.\begin{matrix}C_3H_7\\C_4H_9\end{matrix}\right\}O$.	47	174·7 D		3·71
Di-butyl, $(C_4H_9)_2O$. ..	53	197·7 D		3·73
Averages			22·1	3·68
			6×3·68	

D (Dobereiner).

The Oxidation Products of the Fatty Acids.

The Aldehydes—The CHO *Group.*

Hydrocarbons.

Propaldehyde, $CH_3.CH_2.CHO$, M.V. 74·8
CHO = $C_2H_5CHO - C_2H_5$ =
74·8 − 48·1 .. .. .. = 26·7

Butyraldehyde, $CH_3.CH_2.CH_2CHO$, M.V. = 96
CHO = $C_3H_7CHO - C_3H_7$ =
96 − 70·3 . .. . = 25·7 C_4H_{10} = 96

Valeraldehyde, C_4H_9CHO, M.V. 118·2
CHO = $C_4H_9CHO - C_4H_9$ =
118·2 - 92·5 .. .. .. = 25·7 C_5H_{12} = 117·8

Benzaldehyde, C_6H_5CHO, M.V. = 118·3
CHO = $C_6H_5CHO - C_6H_5$ =
118·3 92·8 .. .. .. = 25·5

Average for CHO group .. = 25·9

Theoretical : (CHO) = 14·8 + 3·7 + 7·4 = 25·9 = 7 × 3·70.

The O″ is equal to 7·4 in the aldehydes as in the alcohols, which is contrary to expectation. It follows that O replaces H_2 in the hydrocarbons without change of volume.

The Ketones—The CO *Group.*

Acetone, $(CH_3)_2CO$, the first member of the group, has an exceptionally large volume, 77·1, as in the cases of form- and acetaldehyde, and also methane and ethane among the hydrocarbons.

Methyl hexyl ketone, $\left.\begin{matrix}CH_3\\C_6H_{13}\end{matrix}\right\}CO$, M.V. 186·64.

C_8H_{18} = 186·26.

Thus, $C_8H_{16}O'' = C_8H_{18}$, O″ = 2H = 7·4

CO = $C_8H_{16}O - C_7H_{16}$ = 186·64 − 162·6 = 24·0.

Pinacolin, $CH_3.CO.C(CH_3)_3$, M.V. 138·5.
C_6H_{14} 139·9.

Here, again, O″ = 2H. CO = 138·5 − 117·8 = 20·7.

The value is slightly smaller than normal because of the tertiary group.

The Fatty Acids—The COOH *Group.*

The fatty acids and mono- and di-carboxylic esters possess volumes such that O″ equals 3H ; that is, the same as in the ethers. The rule is invariable.

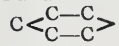
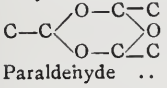
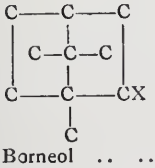
Table XV.

Acids.	W.	M.V.	Δ for CH_2.	V/W.	COOH.
Formic, CH_2O_2 ..	11	41·08	22·82	3·74	37·5
Acetic, $C_2H_4O_2$ ..	17	64·0	22·05	3·76	38·1
Propionic, $C_3H_6O_2$.	23	86·05	23·03	3·74	37·9
Butyric, $C_4H_8O_2$ ..	29	109·08	21·22	3·76	—
Valerianic, $C_5H_{12}O_2$	35	130·3	22·5	3·72	37·8
Caproic, $C_6H_{12}O_2$..	41	152·8	22·2	3·73	38·1
Heptoic, $C_7H_{14}O_2$..	47	175·0	23·2	3·72	38·1
Octoic, $C_8H_{16}O_2$ ..	53	198·2		3·74	—
Averages			22·56	3·74	37·9
			6×3·76		

TABLE XVII.—*Comparison of the Atomic Volumes of* C, H, O *in the Paraffins, Ethers, and Esters.*

Paraffins.	M.V.	−3H.	Ethers.	M.V.	V/W.	Esters (ethyl chiefly).	M.V.	W.	V/W.
C_3H_8 ..	[74]	62·9	C_2H_6O ..	—	—	$C_2H_4O_2$ ..	62·7	17	3·69
C_4H_{10} ..	96·0	84·9	C_3H_8O ..	84·0	3·61	$C_3H_6O_2$ ..	84·7	23	3·68
C_5H_{12} ..	117·8	106·7	$C_4H_{10}O$ ..	106·2	3·66	$C_4H_8O_2$ ..	106·0	29	3·66
C_6H_{14} ..	139·9	128·8	$C_5H_{12}O$ ..	128·1	3·66	$C_5H_{10}O_2$.	128·0	35	3·66
C_7H_{16} ..	162·5	151·5	$C_6H_{14}O$ ..	150·3	3·67	$C_6H_{12}O_2$.	150·9	41	3·68
C_8H_{18} ..	186·2	175·1	$C_7H_{16}O$ ..	174·7	3·72	$C_7H_{14}O_2$.	174·6	47	3·71
			$C_8H_{18}O$ ..	197·7	3·73	$C_8H_{16}O_2$.	197·7	53	3·73
$C_{10}H_{22}$ ..	231·3	220·2	$C_9H_{20}O$ ..	221·1	3·75	$C_9H_{18}O_2$.	221·9	59	3·76
			$C_{10}H_{22}O$ ..	246·1	3·79	$C_{10}H_{20}O_2$.	245·9	65	3·78
			$C_{11}H_{24}O$ ..	271·3	3·82	$C_{11}H_{22}O_2$.	270·3	71	3·81
			$C_{12}H_{26}O$ ..	295·5	3·84	$C_{12}H_{24}O_2$.	295·9	77	3·84
			$C_{13}H_{28}O$ ..	—	—	$C_{13}H_{26}O_2$.	322·6	83	3·89
			$C_{14}H_{30}O$ ..	353·4	3·97	$C_{14}H_{28}O_2$.	351·2	89	3·93
			$C_{15}H_{32}O$ ..	377·6	3·98	$C_{15}H_{30}O_2$.	377·0	95	3·97
			$C_{16}H_{34}O$ ..	404·5	4·00	$C_{16}H_{32}O_2$.	404·3	101	4·00

TABLE XVIII.—*Contractions in Ring Compounds containing Oxygen.*

Substance.	Formula.	M.V.	Σ A.V.	W.	Δ for ring.
Ethylene oxide	C_2H_4O	50	55·5	15	−5·5
Acetaldehyde	C_2H_4O	56·7			
Furfurane	C_4H_4O	73·2	85·1	23	−11·9
Furfural	$C_5H_4O_2$	95·5	107·3	29	−11·8
					
Phenol	C_6H_6O	103·6	118·4	32	−14·8
Benzyl alcohol	C_7H_8O	123·7	140·6	38	−16·9
Carvol	$C_{10}H_{14}O$	190·7	207·2	56	−16·5
Anisol	C_7H_8O	125·2	140·6	38	−15·4
Phenetol	$C_8H_{10}O$	148·5	162·8	44	−14·3
p-Cresyl methyl	$C_8H_{10}O$	147·8	162·8	44	−15·0
Benzoic acid	$C_7H_6O_2$	126·9	144·3	39	−17·4
Dimethyl resorcin	$C_8H_{10}O_2$	153·6	170·2	46	−16·6
Benzaldehyde	C_7H_6O	118·2	133·2	36	−15·0
Phenyl propionic acid	$C_9H_{10}O_2$	170·8	188·7	51	−17·9
Methyl benzoate	$C_8H_8O_2$	150·3	166·5	45	−16·2
Methyl cinnamate	$C_{10}H_{10}O_2$	188·6	203·5	55	−16·9
Methyl phenyl propionate	$C_{10}H_{12}O_2$	196·0	210·9	57	−14·9
Methyl salicylate	$C_8H_8O_3$	157·0	173·9	47	−16·9
Ethyl benzoate	$C_9H_{10}O_2$	174·4	188·7	51	−14·3
					
Paraldehyde	$C_9H_{18}O_3$	151·0	166·5	63	−15·5
			Average contraction		−16·0
					
Borneol	$C_{10}H_{18}O$	190·5	222·0	60	−31·5
Camphor	$C_{10}H_{16}O$	187·4	214·6	58	−27·2

COOH should have a volume $10 \times 3{\cdot}7 = 37$. Thus $O' = 7{\cdot}4$ and $O'' = 11{\cdot}1$.

Acetic anhydride, $(CH_3{\cdot}CO)_2O$ = 109·9. Amylene, C_5H_{10} = 110·0.

$C_4H_6O_3 = C_5H_{10}$. $O_2 - O' = CH_4 - 8H$. Thus, $O' = 2H$ and $O'' = 3H$.

The Aliphatic Esters—Mono-carboxylic.

By analogy it might be expected that $O' = 7{\cdot}4 = H_2$ and $O'' = 11{\cdot}1 = 3H$. This is the case, and thus W is equal to an integral number of H volumes. (See Table XVI.).

The theoretical value of $O_2 = 5 \times 3{\cdot}7 = 18{\cdot}5$.

$O_2 = C_4H_6O_4$ $C_4H_6O_2 = 117{\cdot}5$ $98{\cdot}6 = 18{\cdot}9$.

$CO_2 = 9 \times 3{\cdot}7 = 33{\cdot}3$.

Since COOH from acids = 37·9.

$CO_2 = 37{\cdot}9 - 3{\cdot}7 = 34{\cdot}2$.

So also from dicarboxylic esters:—

$2CO_2 = (COOCH_3)_2 - C_2H_6 = 117{\cdot}5$ $51{\cdot}8 = 65{\cdot}7$. $CO_2 = 32{\cdot}8$.

$2CO_2 = C_5H_8O_4 - C_3H_8 = 139{\cdot}3$ $74{\cdot}0 = 65{\cdot}3$. $CO_2 = 32{\cdot}6$.

The corresponding ethers and monocarboxylic esters in

TABLE XVI.

	W.	M.V.	Δ for CH_2.	V/W.	O_2.
The Esters.					
Methyl formate, $C_2H_4O_2$..	17	62·7	20·5	3·69	18·7
Methyl acetate, $C_3H_6O_2$..	23	83·2	22·8	3·62	17·2
Ethyl ,, $C_4H_8O_2$..	29	106·0	22·8	3·66	18·0
Propyl ,, $C_5H_{10}O_2$..	35	128·8	22·1	3·68	18·8
Butyl ,, $C_6H_{12}O_2$..	41	150·9	22·9	3·68	18·9
Amyl ,, $C_7H_{14}O_2$..	47	173·8	—	3·70	—
Hexyl ,, $C_8H_{16}O_2$..	53	197·7	—	3·73	—
Heptyl ,, $C_9H_{18}O_2$..	59	221·0	—	3·75	—
Octyl ,, $C_{10}H_{20}O_2$.	65	245·8		3·78	—
Unsaturated Esters.					
Allyl acetate, $C_5H_8O_2$ ..	33	121·7	—	3·69	18·5
Methyl acrylate, $C_4H_6O_2$..	27	98·6	—	3·66	—
Ethyl ,, $C_5H_8O_2$..	33	122·0	—	3·70	—
Propyl ,, $C_6H_{10}O_2$.	39	145·3		3·73	—
Dicarboxylic Esters.					
Methyl oxalate, $C_4H_6O_4$ ..	32	117·5	21·8	3·67	2 × 18·0
Methyl ethyl, $C_5H_8O_4$ ..	38	139·3	21·5	3·67	2 × 17·8
Methyl succinate, $C_6H_{10}O_4$	44	160·8		3·65	—
Methyl ethyl, $C_7H_{12}O_4$ ..	50	185·0		3·70	2 × 18·5
Average			22·05	3·69	18·2
			6 × 3·68		

the two series given in Table XVII. show almost identical volumes throughout; as also with series $C_nH_{2n+2} - 3H$.

It thus follows that $C_nH_{2n+2}O = C_nH_{2n}O_2$, and *hydroxyl oxygen*, O′ = 2H throughout the series.

Also $C_nH_{2n+2}O = C_{n+1}H_{2n+4} - 3H$.

Thus, $CH_2 - 3H = 3H = >O$, *ethereal oxygen;* and, consequently, *carboxyl oxygen*, O″ = 3H also.

It is seen that although the identical atomic volumes vary from compound to compound they maintain their relative volumes throughout the series. This has also been shown to be the case with the atoms of the nuclei C_6H_6 and C_6H_{12}, &c., but in these instances a contraction had taken place. *There is thus important experimental evidence in favour of Generalisation* IV. (*q.v.*). Very low boiling-point substances diverge very considerably from the normal, *e.g.*, H_2, O_2, N_2, and in general also the first and second members of each series. This means that at the boiling-point they are not quite comparable with more complex compounds.

Ring Compounds containing Oxygen.

A number of ring compounds have been dealt with in Table XVIII. It will be seen that in conformity with general results previously published (CHEMICAL NEWS, vol. xcix., p. 206) that ring structure is accompanied by a considerable contraction, which varies in magnitude with the size and complexity of the ring. The atoms, however, preserve their usual relative volumes in spite of the contraction.

The contraction is about −6 for three-membered rings.
,, ,, −12 for five membered rings.
,, ,, −15 for six-membered rings.

If the ring becomes more complicated by "bridging," as in the cases of borneol and camphor, the contraction is much increased. Mean about −29·0 (compare Naphthalene, Δ = −30).

Contractions like the above invariably accompany ring structure, and are not a characteristic limited to certain special groups, like the aromatic or hydroaromatic. Thus the volumes of ring compounds—like amylene, C_5H_{10}, and paraldehyde, $C_9H_{18}O_3$—are also marked by similar contractions. The side-chains, being aliphatic residues, possess similar volumes to those of equivalent complexes in straight chain compounds. This is shown to be the case for CH_2 by the method of differences, and, in general, by the fact that the differences ΣA.V. − M.V. are about the same for the same class of compound, whatever be the nature and number of the side-chains. It should be remarked that the value ΣA.V. is equal to the sum of the atomic volumes (or W × 3·7o) of the atoms in the ring compounds, their magnitude being taken as similar to the volumes of like complexes in the aliphatic series. This is a general method, and the difference ΣA.V. - M.V., which measures the contraction, at once indicates what is the nature of the ring structure of the compound.

General Conclusions.

(*a*) The following represent the volumes of the atoms or groups in straight chain compounds or in the side-chains of ring compounds:—

OH .. 11·1 = 3H, COOH = 37·0 = 10H, CO_2 = 33·3 = 9H.
CO″ .. 22·2 - 6H (except carboxylic group in which CO″ = 25·9 = 7H). CHO = 25·9 = 7H.

O′ = 2H in hydroxyl group generally and in phenolic ethers.

O″ = 2H in aldehydes and ketones, O″ = 3H in carboxylic group, exception ethereal O = 3H.

When O enters a ring the volume of >O = 3H.

(*b*) The volumes of ring compounds are marked by contractions, the magnitude of which depends on the size and complexity of the rings.

(To be continued).

REPEATING FIGURES IN THE ATOMIC WEIGHT VALUES.

By F. H. LORING.

An examination of the 1911 atomic weights, including the recent contributions cited in the report of the International Committee, reveals some curious regularities that may be, of course, accidental. There are some notable exceptions. There is an apparent tendency for the figure in the unit's place to recur in the second place of the decimals.

Unfortunately, the second decimal place values are not known with a sufficient degree of accuracy, in most cases, to enable this observation to be put to a rigorous test, but the following table shows what appears to be a tendeney in the direction indicated:—

Ag	107·87	(Richards and Willard)
Ar	39·89	(Fischer and Hahnel)
As	74·94	(instead of 74·96)
Ba	137·37	
Ca	40·10	(instead of 40·09)
Cs	132·82	(instead of 132·81)
Cl	35·454	(Richards and Willard)
Cr	52·02	(instead of 52·01)
Co	58·98	(instead of 58·97)
Fe	55·85	
K	39·09	(instead of 39·10)
Kr	82·92	
Li	6·96	(instead of 6·94)
Mg	24·34	(instead of 24·32)
Mn	54·94	(instead of 54·93)
Ne	20·20	(doubtful)
Ni	58·68	
Ra	226·36	(instead of 226·4; but doubtful)
Rh	102·92	(Reuz). (Dittmar's value, 102·93)
Th	232·42	
Xe	130·20	(instead of 130·22; but doubtful)

Other examples, including Scott's recent (1909), but unconfirmed, value for carbon, might be given. Doubtless

this tendency has been noticed by others. A regularity of this kind cannot obviously exist amongst all the elements without qualification or some expansion of the idea, and, in all probability, if the repetitions hold good, they are limited to certain elements only. Extending this idea of repetitions, silver would be $107\dot{8}78\dot{7}$, and chlorine $35\cdot45\dot{4}5$, and hydrogen, perhaps, $1\cdot00\dot{7}0\dot{7}$.*

It may turn out that the repetitions will not be exact, but only approximate, as in the case of whole numbers. This suggests the notion that the constants of Nature are never exact or ideal in the sense here implied, but closely approximated to, as suggested by an infinite series. This should probably be so by reason of the complex interrelations. No two elements may therefore have *absolutely* the same decimal or repeating fraction, or, indeed, have anything measurable, *absolutely* in common. Such views are, however, debatable.

Like many attempts to bring the constants of Nature into harmony by purely arithmetical means, this one may at best have only a passing interest.

7, Doughty Street, W.C., October, 1910.

SOME TECHNICAL METHODS OF TESTING MISCELLANEOUS SUPPLIES,†

Including Paints and Paint Materials, Inks, Lubricating Oils, Soaps, &c.

By PERCY H WALKER.

(Concluded from p. 220).

Soap.

1. *Sampling.*—It is somewhat difficult to secure a fair sample from a cake of soap, as the moisture content of the outer layer may be very different from that of the interior of the cake. Weigh the whole cake, cut it in two in a diagonal direction, and cut from one of these fresh surfaces in thin layers a sufficient quantity for all determinations, taking care to cut entirely across so as to get a fair proportion of the outer and inner parts. When the cake is not too soft it is sometimes a good plan to run the whole cake through a meat chopper and reduce it all to fine particles. By running through the chopper several times a homogeneous sample is obtained. Preserve the sample in a tightly stoppered bottle and weigh the different portions required as soon as possible.

2. *Moisture.*—The determination of moisture is at best unsatisfactory, and it is better to include it in the "Undetermined." If a determination is required, heat 2 grms. of the finely shaved soap for two hours in an oven at 105° C. The loss is considered as water, though, of course, this is not accurate, as volatile oils may constitute part of the loss, and, on the other hand, all of the water may not be driven off, and if the soap contains free alkali, carbon dioxide will be absorbed from the air. This last source of error may be avoided by drying *in vacuo*. Fahrion's method is much quicker and probably as exact (*Zeit. Angew. Chem.*, 1906, xix., 385). The author states that it gives results within 0·5 per cent of the truth. For this method have a supply of oleic acid which has been heated to 120° with stirring until all of the water is driven off and preserved in a well-stoppered bottle. Weigh from 2 to 4 grms. of the soap in a platinum dish, add three times its weight of oleic acid, and weigh again. Heat the dish cautiously with a small flame until all of the water is driven off and all of the soap is dissolved, being careful not to heat enough to decompose the acid. At the moment when all of the water is driven off the soap forms a clear solution with the acid if there are no fillers present. Cool in a desiccator and weigh. This determination does not require more than fifteen minutes.

3. *Insoluble Matter.*—Dissolve 5 grms. of soap in hot water (use about 75 cc.). Filter on a Gooch or weighed paper and wash with hot water; dry at 105° C., weigh, and calculate the percentage of total insoluble. Ignite the residue and calculate the percentage of insoluble mineral matter.

4. *Total Fatty Matter.*—To the filtrate from the insoluble matter add 40 cc. of half-normal sulphuric acid, heat on the water-bath until the fatty acids have collected in a clear layer on top, cool in ice-water, remove the layer of fatty acids, and wash with water; then heat again with water, cool, remove fatty layer, wash with ice-water, dry with filter-paper, unite the acid liquids, transfer to a separatory funnel, and shake out with two portions of 50 cc. each of gasoline; wash the gasoline twice with 20 cc. of water. Evaporate off the gasoline, add the cake of fatty acids, &c., dry at 100°, and weigh as total fatty matter. This may represent fatty acids, uncombined fat, rosin, and hydrocarbons.

5. *Total Alkali.*—Heat the acid liquid obtained from the determination of total fatty matter to drive off traces of gasoline, cool, add methyl orange, and titrate the excess of acid with fifth-normal alkali. From this titration calculate the amount of acid neutralised by alkali in soap and figure to percentage of sodium monoxide. A more rapid method is to ash the soap, dissolve the ash in water, and titrate. This method gives good results in the absence of silica or other mineral fillers, but cannot be used in their presence.

6. *Free Alkali.*—(a) *Alcoholic Method.*—Treat the freshly cut surface of the soap with a few drops of an alcoholic solution of phenolphthalein; if it does not turn red it may be assumed that free caustic alkali is absent. If free alkali is present, dissolve 2 grms. of the soap in 100 cc. of neutral alcohol (heat is necessary to complete the solution), filter from the undissolved sodium carbonate, &c.; wash with alcohol, add phenolphthalein, titrate with standard acid, and calculate to per cent of free alkali as sodium hydroxide. Should the alcoholic solution be acid instead of alkaline, titrate with standard alkali and calculate the percentage of free fatty acid as oleic acid. Wash the portion insoluble in alcohol with water, add methyl-orange to the washings, and titrate with half-normal sulphuric acid. Calculate to percentage of sodium monoxide present as carbonate, or possibly as borate or silicate. If borax is present boil off the carbon dioxide after neutralising exactly to methyl-orange; cool, add mannite and phenolphthalein, and titrate the boric acid with standard alkali. (b) *Devine's Method.*—The alcohol method of determining free alkali is open to the objection that if the soap contains free alkali and free fat also, by the heating with alcohol the fat will be partly or completely saponified and the free alkali may not be obtainable. Devine's method avoids this danger (*Journ. Am. Chem. Soc.*, 1900, xxii., 693). For this method three standard solutions are used:—(1) Tenth-normal hydrochloric acid; (2) tenth-normal caustic soda or potash in alcohol; (3) tenth-normal stearic acid in alcohol. Solution No. 1 is used to standardise No. 2; Nos. 2 and 3 should be titrated against one another warm, using phenolphthalein as indicator. Weigh 2 grms. of soap (which needs no drying) into a round-bottomed flask of about 300 cc. capacity, and pour 50 cc. of alcohol upon it. Run in sufficient tenth-normal stearic acid from a burette to neutralise the free alkali in 2 grms. of the soap, add some phenolphthalein, and stopper the flask with a cork stopper through which passes a glass tube about

* These repeating tendencies might be indicated thus (as if the decimal point were between the 3 and the 5):—

$$Cl = 35\dot{4}\,;$$

or should some of the repetitions be of a threefold nature, a modification might be introduced thus:—

$$N = 14\cdot00\dot{7}\,;\ C = 12\cdot00\dot{3}\,;\ H = 1\cdot00\dot{8}.$$

Of course it is beyond the scope of present-day experiment to determine atomic weights accurately in the sixth place of the decimals, and therefore such representations are devoid of interest, except in so far as they amplify the idea founded on the second decimal place coincidences.

† *Bulletin* No. 109, Revised, U.S. Department of Agriculture, Bureau of Chemistry.

30 inches long and of about ¼ inch internal diameter, having the lower end ground to a point on a grindstone. The purpose of the tube is to serve as a reflux condenser. Place the flask and contents on a steam-bath, and heat for thirty minutes. At the expiration of this time the solution should be quite clear and show no alkali with the phenolphthalein. If the solution turns red during the boiling, showing that an insufficient quantity of stearic acid has been added at first, add more of that solution until the colour disappears, then several cubic centimetres in excess, and heat twenty minutes longer. Remove the flask from the bath, and, after cooling it a few minutes, titrate with tenth-normal caustic soda. The difference between the number of cubic centimetres of stearic acid solution added and the number of cubic centimetres of caustic soda used to neutralise it is equivalent to the total free alkali present. While the first flask is heating, weigh in a similar flask 2 grms. of soap, add 50 cc. of alcohol, and place on the steam-bath. When the first test is finished, calculate roughly the total alkali, assuming the total quantity to be carbonate. Now add to the second flask sufficient 10 per cent barium chloride solution to precipitate the alkali found, heat a few minutes, add phenolphthalein, and titrate with tenth-normal stearic acid. (One cc. of tenth-normal stearic acid corresponds to 0·0122 grm. $BaCl_2.2H_2O$ or 0·122 cc. of a 10 per cent barium chloride solution). The titration must take place slowly and with thorough agitation of the liquid because the sodium or potassium hydroxide reacts with the barium chloride added and forms sodium chloride and barium hydroxide. The latter is not very soluble in the alcoholic liquid, and sufficient time and pains must be taken to insure its complete neutralisation by the stearic acid. Make a blank test on 50 cc. of the alcohol, since this frequently contains carbon dioxide, and add the amount of tenth-normal caustic soda necessary to neutralise the free acid in this quantity of alcohol to the reading of the stearic acid burette in the second test. This corrected reading gives the number of cubic centimetres of tenth-normal stearic acid used to neutralise the caustic alkali in 2 grms. of soap. The difference between the total alkali found and the caustic soda will, of course, give the carbonate. For example: To 2 grms. of soap and 15 cc. of tenth-normal stearic acid add 3·2 cc. of tenth-normal caustic soda to neutralise. Then 15 cc. − 3·2 cc. = 11·8 cc. of tenth-normal stearic acid equivalent to total free alkali. To neutralise the caustic soda in the sample treated with barium chloride 4·1 cc. of tenth-normal stearic acid was required. Fifty cc. of the alcohol used required 0·2 cc. of tenth-normal caustic soda, hence the total is 4·3 cc. Since it requires 4·3 cc. of tenth-normal stearic acid to neutralise free caustic alkali, 11·8 cc. − 4·3 cc. = 7·5 cc. of tenth-normal stearic acid required to neutralise the carbonated alkali. One cc. of tenth-normal stearic acid = 0·004 grm. of caustic soda or 0·0053 grm. of sodium carbonate. These figures calculated to percentage would be: 0·86 per cent of caustic soda and 1·99 per cent of sodium carbonate. It is to be noted that a rubber stopper cannot be used in the flasks used for dissolving the soap on account of the sulphur in the rubber which decolorises an alcoholic solution of phenolphthalein. The method is applicable to all soaps that do not contain fillers which react with the standard solutions employed.

7. *Unsaponified Matter.*—Dissolve 5 grms. of soap in 50 cc. of 50 per cent alcohol; if any free fatty acids are present add just enough standard alkali to neutralise them, and wash into a separatory funnel with 50 per cent alcohol. Extract with 100 cc. of gasoline (B.P. 50—60°). Wash the gasoline with water, evaporate, and weigh as unsaponified. This may consist of fat that has not been converted into soap or of hydrocarbon oils.

8. *Rosin.*—If much unsaponified matter is present, prepare dry fatty and rosin acids from the portion from which the unsaponified matter has been removed. Dissolve 3 grms. of the dry mixed acids in 25 cc. of absolute alcohol in a 100 cc. stoppered flask, place the flask in cold water and shake; add 25 cc. of absolute alcohol saturated with dry hydrochloric acid, shake occasionally, and let the action go on for twenty minutes; then add 10 grms. of dry granular zinc chloride, shake, and allow to stand for twenty minutes. Pour the contents of the flask into 200 cc. of water in a 500 cc. beaker, and rinse out the flask with dilute alcohol. Put a small stick of metallic zinc in the beaker and boil off the alcohol. Cool, transfer to a separatory funnel, extract with gasoline, wash the gasoline until free from hydrochloric acid, distil off the gasoline, dissolve in neutral alcohol, and titrate with standard alkali, using phenolphthalein as indicator. (One cc. of normal alkali corresponds to 0·346 grm. of rosin). The rosin may be determined gravimetrically by washing the gasoline extract with water. It is not necessary to wash absolutely free from acid. Then treat the extract in the funnel with a solution of 5 grms. of potassium hydroxide and 5 cc. of alcohol in 50 cc. of water. Upon shaking, the rosin is rapidly saponified and the two layers separate well. Draw off the rosin soap, wash the gasoline once with water, add the washings to the soap solution, add an excess of acid, extract the rosin with gasoline, evaporate the gasoline, and weigh the rosin.

9. *Silica and Silicates.*—Insoluble silicates, sand, &c., are present in the insoluble; but sodium silicate fillers will only show by forming pasty liquids. When sodium silicate is suspected, ash the soap (10 grms.), add an excess of hydrochloric acid to the ash, evaporate to dryness; add hydrochloric acid and again evaporate to dryness; cool, moisten with hydrochloric acid, dissolve in water, filter, wash, evaporate the filtrate to dryness, and again take up with hydrochloric acid and water, filter, and wash. Unite the precipitates, ignite, and weigh as silicon dioxide; calculate to sodium silicate ($Na_2Si_4O_9$). If metals other than the alkalis are suspected, the filtrate from the silica determination may be examined.

10. *Glycerin.*—Dissolve 20 to 25 grms. of soap in hot water, add a slight excess of sulphuric acid, and heat on a water-bath until the fatty acids separate in a clear layer. Remove the fatty acids and filter the acid solution into a graduated flask. Remove the chlorides and the soluble fatty acids by adding crystals of silver sulphate, cool, make up to the mark, mix, allow to settle, filter through dry paper, take an aliquot corresponding to 5 grms. of soap, and determine by Hehner's bichromate method (see under Glycerin). This method cannot be used when sugar is present as it also would reduce the bichromate. When sugar is present, remove the fatty acids as just described, neutralise an aliquot with milk of lime, evaporate to about 10 cc., add 2 grms. of sand and milk of lime containing about 2 grms. of calcium hydroxide, and evaporate almost to dryness. Treat the moist residue with 5 cc. of 96 per cent alcohol, rub the whole mass into a paste, heat the mixture on a water-bath, stirring constantly, and decant the liquid into a 250 cc. flask, wash the residue five or six times with small portions of alcohol, cool the contents of the flask to 15°, fill to the mark with 96 per cent alcohol, mix, and filter through a dry paper; evaporate 200 cc. of the filtrate to a syrupy consistency on a water-bath, transfer to a stoppered cylinder with 20 cc. of absolute alcohol, add three portions of 10 cc. each of absolute ether, mixing after each addition; let stand until clear, pour off through a filter, and wash the cylinder on the filter with a mixture of two parts of absolute alcohol and three parts of absolute ether. Evaporate to a syrup, dry for one hour at the temperature of boiling water, weigh, ignite, and weigh again. The loss multiplied by five-fourths is the weight of the glycerin in the aliquot taken. Instead of weighing the glycerin it can be titrated after driving off the alcohol and ether.

11. *Sugar.*—Dissolve 5 grms. of soap in water, add an excess of hydrochloric acid, heat on a steam-bath for thirty minutes, cool, separate the fatty acids, and make up to a definite volume. Add an aliquot, depending upon the amount of sugar supposed to be present, to 50 cc. of a mixed Soxhlet solution, make the total volume 100 cc.,

heat to boiling, boil two minutes, filter on a weighed Gooch, wash with water, then with alcohol and ether, dry at 100° for thirty minutes, cool, and weigh the cuprous oxide. Calculate the percentage of sugar as invert sugar according to Munson and Walker's tables (*Journ. Am. Chem. Soc.*, 1906, xxviii., 663).

THE ATOMIC WEIGHT OF MERCURY.*

(Second Paper).

By C. W. EASLEY.

In a series of experiments on the atomic weight of mercury, described in a previous communication (*Journ. Am. Chem. Soc.*, xxxi., 1207), mercuric chloride of very great purity was prepared, and its analysis tended to show that the accepted value of this constant was too low. This conclusion was reached as a result of work having to do with the ratio $HgCl_2 : 2AgCl$. Since the results differ from the accepted value by three-tenths of 1 per cent, it seemed best to establish their correctness in a general way before publication. This was done by determining the percentage of mercury in mercuric chloride, but it was explicitly stated that the method of verification was involved, and did not approach in accuracy the one by which the ratio $HgCl_2 : 2AgCl$ was determined, and that the former was employed merely to indicate the general neighbourhood in which the true value lay. The value obtained by this, less accurate method, differed from the first by less than one-tenth of 1 per cent, but the process was so questionable from the standpoint of the complete collection of the mercury that the same ratio has been determined in another way by work in the laboratory of the University of Maine.

(Note.—That a small portion of the finely divided metal passed by the filter in the process of its separation from the filtrate containing the chlorine was known from the solvent action of the mercury salt on the silver chloride. This was described in the previous paper. In fact, only a few of the attempts to collect and determine the mercury were successful, owing to its tendency, under the conditions of the experiments, to be precipitated in such a finely divided state).

The results corroborate and agree very closely with the higher value previously published. To determine this ratio, the metal was deposited electrolytically from mercuric chloride of the same degree of purity as that employed in the previous work, the methods of preparation being identical. The value obtained, 200·63, is in almost exact agreement with the finding of the previous investigation, 200·62, calculated from the ratio $HgCl_2 : 2AgCl$, which was believed to give a result with very small error.

Historical and Critical Survey.

In order to find a possible source of error in the work of previous investigators, it may be best to append the work already published.

The table brings to light the fact that mercury itself constitutes one term of every ratio. The metal has been liberated from the several compounds by two methods :— (1) By heating with calcium oxide or copper in a stream of an inert gas by means of which the mercury was swept out of the tube containing the reacting mixture, the vapour being condensed in a portion of the apparatus used subsequently for weighing the deposit; (2) by depositing the metal on a platinum dish with the aid of the electric current. It is not unlikely that the first method is subject to loss of mercury through imperfect condensation, as it will be shown later that the vapour pressure of mercury at rather low temperatures, although small, is sufficient to be of considerable importance. This would seem to be the main point of weakness in all the previous work, as the preparation of the compounds in a fairly pure condition, with the exception of the oxide, appears to be a comparatively simple matter. (It was shown in the previous paper that the sublimation of the chloride from material containing water, such as re-crystallised salt, is attended with the production of a slight amount of basic salt). Whether any of the compounds escaped contact with the lime or copper, however, might be questioned. The process was certainly complete in the electrolytic method of Hardin, but the details concerning such an important matter as the drying of the deposit are so meagre that the results do not carry the weight that their agreement would otherwise warrant.

	Ratio.	At. wt.
Turner (*Phil Trans.*, 1833, p. 531)	HgO : Hg	200·63
Erdmann and Marchand (*Journ. Prakt. Chem.* xxxi., 395) ..	HgO : Hg	200·20
Hardin (*Journ. Am. Chem. Soc.*, xviii., 1003)	HgO : Hg	200·04
Erdmann and Marchand (*Journ. Prakt. Chem.*, xxxi., 395) ..	HgS : Hg	200·52
Turner (*Phil. Trans.*, 1833, p. 531)	$HgCl_2$: Hg	199·67
Millon (*Ann. Chim. Phys.*, xviii., 345)	$HgCl_2$: Hg	200·22
Svanberg (*Journ. Prakt. Chem.*, xlv., 472	$HgCl_2$: Hg	199·71
Hardin (*Journ. Am. Chem. Soc.*, xviii., 1903)	$HgCl_2$: Hg	200·06
Hardin (*Journ. Am. Chem. Soc.*, xviii., 1903)	$HgBr_2$: Hg	199·80
Hardin (*Journ. Am. Chem. Soc.*, xviii., 1903)	$Hg(CN)_2$: Hg	199·84
Hardin (*Journ. Am. Chem. Soc.*, xviii., 1903)	Hg : Ag	199·92
Turner (*Phil. Trans.*, 1833, p. 531)	$HgCl_2 : 2AgCl$ (*a*)	—

(*a*) In this determination, no account whatsoever was taken of the solvent action of mercury salts on silver chloride, so that the values have been excluded from the table as being subject to known error; the results were abnormally high.

The loss of mercury at low temperatures due to its vapour pressure, however slight, is not to be overlooked. At a given temperature, the loss would obviously depend upon the rate at which the vapour was swept through the condensing tube, or, in the case of drying deposits on platinum dishes, on the amount of convection currents in the immediate neighbourhood. In the first case, it is entirely possible that the condensation of the mercury, its partial pressure in the mixture being small, from the stream of hot gas was not complete in spite of the fact that gold leaf was employed to collect the portions which might escape. The question involved in the later electrolytic work is the same, but here we have to do with the metal spread over the surface of a dish which "was washed several times with boiling water and carefully dried." The temperature and method of drying are not stated.

It is well-nigh impossible to reproduce the exact conditions under which various observers have worked, but some experiments were undertaken to show the effect of evaporation at moderately low temperatures on the weight of mercury. However, no attempts at exaggerating the ordinary drying methods were made. Instead of exposing a considerable surface of the metal such as a deposit on a dish, a globule of dry mercury having a surface of 1·5 sq. cm. was placed in a weighing bottle 3 sq. cm. in cross section, and 5 cm. in height. The bottle was placed in an air oven, and maintained for such periods of time and at such temperatures as are shown in the accompanying table. Under such conditions there are no air currents to

* From the *Journal of the American Chemical Society*, xxxii. No. 10.

any extent, and no other liquid whose vaporisation would tend to carry away the mercurial vapour with it.

Hours in oven.	Temperature of oven.	Total loss in grms.	Loss in grms. per hour.
3	50°	0·0016	0·00053
4½	50	0·0024	0·00053
10	50	0·0033	0·00033
6	50	0·0027	0·00048
3½	50	0·0010	0·00029
19	50	0·0057	0·00030
8	60	0·0050	0·00063

The results are as concordant as one might expect, and even under these conditions, where the evaporation is reduced to a minimum, the loss is considerable. Especially in the case of a mercury deposit on a platinum dish,* the effect is not to be neglected because of the relatively large error† due to the small amount of mercury which may be satisfactorily dealt with in this manner.

In the following work, in view of the errors which might arise from the volatility of the metal, it was decided to dry the mercury at ordinary temperatures, using acetone to remove the water as was done in the previous work. The error committed by this procedure is exceedingly small, although under favourable conditions the evaporation of mercury may be measured at quite low temperatures. Thus, in a room subject to draughts, at a temperature of 25°, a slight though decided loss was noticed on several occasions when a considerable surface of mercury was exposed for twenty-four hours.

General Method.

In order to secure recognition of the higher value of the atomic weight of mercury by any method, the latter must be free from the objections urged against the process used in determining the same ratio as described in the preliminary paper (*Journ. Am. Chem. Soc.*, xxxi., 1207). The electro-deposition of mercury from the chloride under proper conditions realises this condition to a marked degree. That the metal is completely freed from the chlorine by this process is well known, and its complete collection is assured from the form of the apparatus. Again, electrolytic methods in general possess simplicity. In the work here described even greater simplicity, and therefore greater accuracy, has been attained from the manner in which the deposit is handled. A special vessel was devised in which the metal was deposited in globular form by means of a mercury cathode, and without being removed was washed by decantation, freed from water by means of acetone, and finally weighed. A test of the method is whether a globule of mercury can be subjected to the above-mentioned treatment without change of weight. Many experiments bearing on this point show that the changes in weight, a similar vessel receiving similar treatment, of course, serving as a counterpoise, are small, never being greater than a tenth of a mgrm. and generally no more than a few hundredths. Such changes may therefore be attributed to errors incident to weighing glass vessels of the size employed. By the electrolysis of known weights of mercuric chloride with precautions to be mentioned later, one has a method at once simple and accurate and possessing the very great advantage, other things being equal, that relatively large amounts of mercury may be deposited without increasing the error of measurement. Over 20 grms. of mercuric chloride were electrolysed in the tube with the same ease and accuracy as were the smaller amounts.

The Material.—For the sake of comparison with the work previously published, three samples of mercuric chloride were prepared with the same care and in precisely the same manner as in that work. For the details reference should be made to that paper. The corresponding samples are designated by the same numbers in both communications. The analyses of these samples are considered in a series by themselves for the reason that no suspicion whatever is attached to the purity of either the salt or the mercury obtained from it.

Not so much can be claimed for Sample o which was originally intended for the preliminary work in order that some uniformity of results might be attained while the method was being tested out. To this end, the choicest appearing crystals from Kahlbaum's highest grade of mercuric chloride were sublimed in a current of dry air in the special tube described in the previous paper. A large fraction coming over first was discarded, but most of the remainder was collected. During the sublimation the temperature was maintained in the neighbourhood of 300°. An exceedingly small residue, for commercial material, remained, which had every appearance of being carbon. The salt was entirely soluble in water.

The results of the analyses of this sample were quite concordant, and a search was begun to discover the nature of the traces of impurities, for it was evident that very pure salt was being dealt with. Slight amounts of arsenic only could be found in the original Kahlbaum salt and none whatever in the sublimed portion, so that it was decided to use the results of the analyses of this sample as evidence in this investigation. Naturally, less weight must be attached to the results from this sample, subjected to physical treatment only in its purification, than to the values from Samples 1, 2, and 3, especially as the latter samples were the last to be analysed, and thus greater manipulative skill was possible at this stage of the work. That some impurity was present, however, was evidenced from the fact that the globule after drying had a peculiarly striated appearance here and there, although the surface was lustrous. Any metal deposited simultaneously must have been present in very small amounts, and would probably have dissolved in the mercury. The deposition of platinum was not the cause, for the same phenomenon did not occur with any of the other samples. Judging from the high results, if a foreign metal is present, it must have an atomic weight higher than that of mercury, which is quite improbable. The sample gives a result so little above that of the final series, however, that the difference might be accounted for by the retention of a minute quantity of water or even acetone by the peculiar surface which, in turn, might have been caused by the slightest amount of an impurity.

(Note.—That the presence of very small amounts of certain impurities interferes with the tendency of the separate particles to unite is well known. In washing the mercury obtained from this sample, the particles sometimes became detached, and considerable more difficulty was experienced in reuniting them than in the case of the other samples. It is not impossible that a small amount of packing material, often found in chemicals, was destroyed during the sublimation, and that some of the products distilled over, so that the appearance of the mercury might be due to very small detached particles of the metal itself covered with a film of organic matter).

Weighing.—A Sartorius balance was used, and the consecutive weighings could be relied upon to one-fortieth of a mgrm. In determining the weight of the salt, substitution was the method employed, while, in the case of the mercury, the tube containing the metal was counterpoised with a similar tube, and was subjected to the process of double weighing in order to correct for the inequalities in the length of the balance arms.

The gold-plated brass weights were calibrated and the proper corrections applied. The following vacuum corrections were made:—

+ 0·000080 grm. per grm. of mercuric chloride.
− 0·000055 grm. per grm. of mercury.

* The manuals on electro-analysis do not agree on the temperature at which mercury should be free from water. One commonly used, however, recommends the drying on a moderately warm plate.

† Thus, with 1 grm. of mercuric chloride, the average amount used by Hardin, each change of a tenth of a mgrm. of the metal in the neighbourhood of the actual amount present affects the atomic weight in the first decimal place.

The Cathode.—In view of the difficulties attending washing and drying deposits on platinum dishes, it was decided very early in the course of the work to make use of a mercury cathode, an idea due to Wolcott Gibbs in 1883 (*Am. Chem. Journ.*, xiii., 571), and used by him and others in depositing various metals in the form of amalgams. The main drawback to the more general adoption of such a method has been the difficulty of handling the deposit, an objection which has been overcome in this work. In the present case, such a cathode seems ideal in that it avoids an interface of any considerable area with another conducting surface, with the consequent questionable procedure of washing and drying under such circumstances. Again, one is not limited to the deposition of very small amounts of metal, which amounts cannot be exceeded in using platinum dishes, owing to the tendency of the mercury to collect in drops at the bottom of the dish; nor does the question of current density arise to change the nature of the deposit.

To discover whether or not hydrogen was retained by the mercury, a dilute solution of hydrochloric acid in one case and of sulphuric acid in another was electrolysed, and the effect on the weight of the cathode was determined. In one of the experiments only was there an increase in weight, so that the change in this exceptional case was considered accidental. Had this effect been caused by hydrogen, the atomic weight of mercury would have been changed only one unit in the second decimal place.

For the electrode, 5 to 10 grms. of mercury, prepared by the reduction of pure mercuric chloride, was placed in the electrolysing tube in contact with the platinum wire. The mercury was first washed with water, treated with acetone, and dried with air, as will be described later. At the conclusion of some of the experiments, a portion of the deposited metal was retained to serve as a cathode, thereby effecting a saving in the preparation of pure mercury. The globule constituting the cathode always possessed a clean lustrous surface.

(To be continued).

NOTICES OF BOOKS.

The Theory of Ionisation of Gases by Collision. By John S. Townsend, M.A., F.R.S. London: Constable and Company, Ltd. 1910.

The author of this book has done much valuable work in connection with the experimental study of the conductivity of gases through which ions are passing, and his theory of ionisation by collision affords a satisfactory explanation of the phenomena observed. A complete discussion from his pen of this theory will be welcomed by investigators who are working on the same lines, and who have found it difficult hitherto to harmonise the somewhat conflicting information to be found scattered in original papers throughout various periodicals which have appeared during the last ten years. The treatment of the subject is very clear and systematic, ionisation by negative ions being first discussed, with methods of determining the value of α from experiments with Röntgen rays and ultra-violet light. Then ionisation by positive ions is considered, and the theory of electric discharges both in a uniform and a non-uniform field of force is explained in two excellently clear chapters.

A Text-book of Physical Chemistry Theory and Practice. By Arthur W. Ewell, Ph.D. London: J. and A. Churchill. 1910.

The experiments described in this book for laboratory practice are fairly advanced, while the theory of physical chemistry is treated from a point of view which is distinctly above that of the average student beginning a first year's college course. A good deal of matter is included which properly belongs to physics; for instance, much of the work on light, although the author has always emphasised the study of such phenomena as are of special interest and importance to students of chemistry. In the same way the introduction includes the discussion of such subjects as the calculation of errors and even abbreviated methods of calculation which really belong to mathematics and should be unnecessary in a text-book of physical chemistry. The various forms of apparatus which are employed in the physical chemistry laboratory are well described, and the course of practical work outlined is very comprehensive, and should give the student a thorough knowledge of his subject. The theoretical discussions are clear, and are so arranged that although the use of the calculus is introduced, it is not absolutely essential for the student to have mastered its principles in order to follow the text. The questions and problems are an excellent feature of the book; they should stimulate thought and encourage initiative, and the student who can cope with them successfully may be regarded as thoroughly efficient.

A Manual of Elementary Practical Chemistry. By P. W. Oscroft, M.A. (Cantab), and R. P. Shea, M.A. (Oxon.). London: Rivingtons. 1910.

Although the authors claim for this book a certain novelty in the arrangement of the experiments which they believe to add to its value, the alteration can hardly be described as entirely for the better. For instance, it would be wiser to defer the study of the halogens and their acids until the student had some knowledge of the general properties of acids, bases, and salts. On the other hand, some new experiments are described, and the directions are in all cases clear and concise. Elementary volumetric work is included, and many teachers will agree with the authors' estimate of the value of the training obtained by learning to analyse a simple salt, and will welcome the excellent directions given for the performance of a simple analysis for bases and acids.

The Battersea Polytechnic Magazine, July, 1910.

The July number of this magazine contains, besides notices and reports which are of interest chiefly to past and present students, two articles on scientific subjects. The first, on the House Fly, is based upon papers published in the *Quarterly Journal of Microscopical Science* and in other journals by Dr. C. G. Hewitt, and the second deals with the discharge of electricity through high *vacua*, which has been the subject of a thorough research by Mr. S. Marsh.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Zeitschrift für Anorganische Chemie.
Vol. lxvii., No. 4.

4 : 3-Basic Zirconium Sulphate and its Hydrates.—Otto Hauser and H. Herzfeld.—The authors' researches show that the two hydrates $4ZrO_2.3SO_2.15H_2O$ and $4ZrO_2.3SO_2.7H_2O$ exist as definite chemical compounds, while there are no intermediate hydrates, dehydration between the two compounds giving mixtures only. When basic zirconium sulphate is dehydrated at about 300° the anhydride is obtained in the form of a beautiful white crystalline mass, which is apparently pseudomorphous with the hydrate with $15H_2O$. Its specific gravity is 4·1. No loss of sulphuric acid occurs when the water is driven off, and the product has a perfectly constant composition its formula being $Zr_4O_5(SO_4)_3$.

Double Bromides of Manganese.—Fritz Ephraim and Samuel Model.—Only one double bromide of manganese is known, viz., $MgMnBr_4.12H_2O$. Manganese bromide shows only a very slight tendency to form double bromides, and in this respect resembles cobalt bromide. The authors could not obtain any salts with potassium, barium, or strontium bromides, but have prepared a calcium manganous bromide, $CaMnBr_4.4H_2O$. It is a compound

which is not quite stable even at room temperature, but shows a tendency to decompose into its constituents.

Double Chlorides and Iodides of Zinc.—Fritz Ephraim and Samuel Model.—The following double chlorides and iodides of zinc exist:—$CaZnCl_4.5{\cdot}5H_2O$, $Ca_2ZnCl_6.6H_2O$, $SrCl_2.ZnCl_2.4H_2O$, $BaZnCl_4.4H_2O$, $KZnI_3$, $K_2ZnCl_4.2H_2O$, $Na_2ZnI_4.3H_2O$, $NaZnI_3.2H_2O$, $(NH_4)_2ZnI_4$, $NH_4ZnI_3.aq$, $CaZnI_4.8H_2O$, $SrZnI_4.9H_2O$, $BaZnI_4.4H_2O$.

Conduction of Electricity in Crystals at High Temperatures.—C. Doelter.—Crystals can be classified into the following groups:—(A) Those such as lead glance, iron glance, magnetic iron pyrites, which at all temperatures exhibit electronic but not ionic conduction, but which may perhaps conduct ionically at high temperatures. (B) Crystals which are insulators at the ordinary temperature but which conduct metallically at temperatures from 400—500°, *e.g.*, molybdenum glance, antimony glance, fahlore, zinc blende, wolframite. (C) Crystals such as tin-stone, chrysoberyl, and probably quartz, in which both kinds of conduction occur at high temperatures. (D) Crystals which are insulators at the ordinary temperature, but at high temperatures are good electrolytic conductors and show decided polarisation, *e.g.*, sapphire, the silicates, barytes.

Estimation of Hydroferro- and Hydroferricyanic Acids.—Erich Müller and Otto Diefenthäler.—Two methods of determining hydroferro- and hydroferricyanic acid are in use, viz., titration of the aqueous solution with permanganate and iodometric determination. The authors have investigated the different modifications of these methods, and have found that de Haen's method of titration with permanganate gives accurate results, and that the determination of hydroferricyanic acid with permanganate after reduction with ferrous sulphate is also accurate. Rupp and Schiedt's process for determining hydroferrocyanic acid by the addition of excess of iodine solution and back titration of the excess with thiosulphate in alkaline bicarbonate solution gives values which are 1 to 2 per cent too low. The determination of hydroferricyanic acid by Mohr's method gives satisfactory results if it is performed as follows:—About 0·7 grm. of ferricyanide is dissolved in 50 cc. of water, 3 grms. of potassium iodide are added, and 1·5 grm. of zinc sulphate free from iron, and the iodine is titrated at once, after shaking with 1/20-N-thiosulphate solution and starch. If the solution of ferricyanide is acid it must be neutralised.

Solubility of Alkali Sulphates in Solutions containing Alkali at 25°.—J. D'Ans and O. Schreiner.—Increasing amounts of caustic soda were introduced into a saturated solution of $Na_2SO_4.10H_2O$ at 25°, and the solutions were then analysed. It was found that the solubility of sodium sulphate is lowered by increasing quantities of free alkali. The same result was obtained with potassium sulphate and ammonium sulphate. When gypsum was introduced into these solutions it was observed that when the concentration in free alkali was high $Ca(OH)_2$ was the stable substance, except with ammonium sulphate.

Gold-magnesium Alloys.—G. G. Urasow and Rudolf Vogel.—From the study of the concentration-temperature curves of mixtures of gold and magnesium it has been found that Urasow's compound, Au_2Mg_5, exists, but it is stable only between 716° and 796°.

Use of Potassium Ferricyanide in Alkaline Solution to Determine Vanadium and Chromium.—Howard E. Palmer.—The method depends upon the oxidising action of potassium ferricyanide in alkaline solution, the resulting ferrocyanide being oxidised by permanganate in acid solution. The following equations represent the reactions:—

$$V_2O_4 + 2K_3Fe(CN)_6 + 2KOH = V_2O_5 + 2K_4Fe(CN)_6 + H_2O.$$

$$Cr_2O_3 + 6K_3Fe(CN)_6 + 6KOH = 2CrO_3 + 6K_4Fe(CN)_6 + 3H_2O$$

$$5K_4Fe(CN)_6 + KMnO_7 + 4H_2SO_4 = 5K_3Fe(CN)_6 + 3K_2SO_4 + MnSO_4 + 4H_2O.$$

MISCELLANEOUS.

Prizes for the Solution of Technical Problems.—The Council of the Society of Dyers and Colourists have pleasure in offering prizes for the solution of the technical problems specified below. It is hoped that this prize scheme will prove of value to the progress of the dyeing and allied industries, and will stimulate research.

Prize of £15 for a full investigation of the relative affinity for cotton of the tannins of galls, myrabolams, sumach, divi-divi, and quebracho, and the relative fastness to light and washing of the colour lakes produced with these tannins and basic colours, in conjunction with antimony, tin, and iron.

The Silver or Bronze Medal of the Society for a satisfactory method of determining by volumetric or other means of analysis the relative mordanting values for cotton of different tannin materials.

The Silver or Bronze Medal of the Society for the best critical essay (not exceeding 10,000 words) on the treatment of effluents from dyehouses and textile factories.

Prize of £20 for a determination of the average degree of diminution in strength, if any, of a standard cotton yarn, either American, Egyptian, or Sea Island, brought about by different processes of bleaching under good practical working conditions.

Prize of £30 for a practical method of causing kemps, when present in yarn or piece goods, to take dye-stuffs equally with the accompanying wool.

Prize of £20 for a practical method of dyeing on cotton full shades of basic colours which are fast to rubbing.

Prize of £20 for a practical method of dyeing a black on cotton yarn to stand a chlorine bleach, and to be fast to rubbing, and at a cost not exceeding that of an ordinary aniline oil black.

Prize of £10 for a satisfactory method of rendering acid colours soluble in hydrocarbon oils for use in "dry dyeing."

Prize of £15 for a satisfactory investigation on the effects of fermentation on the sizing properties of flour.

Prize of £5 for a rapid and sufficiently exact method of estimating sodium sulphide in a standing bath of a sulphide dye.

Prize of £20 for a satisfactory method of preventing in calico printing the marking off of "extract" colours during open steaming so as to do away with the present necessity of using "greys."

Prize of £20 for a printing machine cylinder that would do away with the necessity of using lapping, back greys, or blankets.

All papers, &c., sent in for competition must be delivered free to the Honorary Secretary of the Society, on or before June 30th, 1911.—ERNEST T. HOLDSWORTH, Hon. Sec., Pearl Assurance Buildings, Market Street, Bradford.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Relation of Metallurgy to Chemical Industry," by A. C. Claudet.

THURSDAY, 10th.—Royal Society. "Tidal Observations of the British Antarctic Expedition of 1907," by Sir George Darwin. "Conduction of Heat through Rarefied Gases," by F. Soddy and A. J. Berry. "Chemical Physics involved in the Precipitation of free Carbon from the Alloys of the Iron-carbon System," by W. H. Hatfield. "Determination of the Tension of a Recently-formed Water Surface," by N. Bohr.

FRIDAY, 11th.—Physical 8. "Supposed Propagation of Equatorial Magnetic Disturbances with Velocities of the Order of 100 Miles per Second," by C. Chree. "Cusped Waves of Light and the Theory of the Rainbow," by W. B. Morton. Exhibition of a Brightness Photometer, by J. S. Dow.

THE CHEMICAL NEWS.

Vol. CII., No. 2659.

THE ATOMIC WEIGHT OF MERCURY.*

(Second Paper).

By C. W. EASLEY.

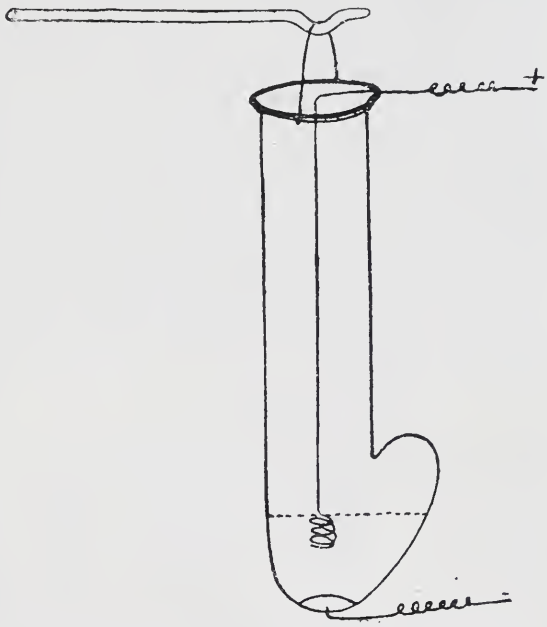
(Concluded rom p. 232).

The Anode. — As concentrated solutions of mercuric chloride were to be electrolysed with the consequent production of strong chlorine solutions, considerable time was spent in search for suitable anode material, for it was expected that platinum would be strongly attacked. Carbon in several of its forms was tried, but it was not to be relied upon, either because of its absorptive properties or because of the tendency of portions to become detached. Again, such electrodes are difficult to treat in such a manner that constant weight is maintained, and thus one has no check on this important point. In describing a method of overcoming the solvent effect of chlorine on a rotating platinum anode, Smith recommends the use of a layer of toluene or xylene on the solution just above the anode ("Electro-analysis"). This was tested, although in this work the anode was stationary, with the result, as afterward found, that more of the platinum was dissolved by this treatment than without the absorptive layer. It was therefore decided to use the platinum, as is ordinarily done, find its loss of weight, determine the amount in the solution after the electrolysis, and thus calculate by difference the amount deposited with the mercury. Contrary to expectations, the loss of platinum by solution was exceedingly small, and practically all of the dissolved portion was deposited with the mercury, none being found in solution at the conclusion of an experiment. The anode at the beginning of the experiments described later weighed 1·54895 grms., and at their conclusion 1·54880; or, during the course of eleven experiments in which over 125 grms. of mercuric chloride had been electrolysed, the anode lost 0·00015 grm.

The platinum wire, weighing 1·5 grms. and having a length of 35 cm., was wound at one end into a spiral, the latter being maintained at approximately 2 cm. from the cathode. The other end of the wire was connected with the battery terminal by means of a clip.

The Electrolysing Tube.—The figure illustrates the essential features of this vessel, which was constructed of glass tubing of about 30 mm. diameter. The tube, 160 mm. in length, was closed at one end, and a bulb was blown into its side near the bottom. The tube could thus be inverted in such a manner that the mercury remained in the bulb, and by careful manipulation practically all of the supernatant liquid could be removed. When filled to the top of the bulb, the tube had a capacity of approximately 50 cc. Through the bottom was sealed a piece of platinum wire which projected on the inside just far enough to make contact with the mercury cathode. As the vessel was to remain unaltered in weight during its subsequent treatment, save for the mercury deposited, all portions of the surface were carefully smoothed in the flame. To this same end, the platinum wire was connected with the battery terminal by means of a clip which precluded any abrasion of the surface of the platinum. For convenience during the processes of electrolysis and weighing, a platinum wire was wound about the neck of the tube to serve as a loop for suspension. During the former process, the tube hung on a glass rod; in weighing, the hooks on the balance arms were utilised as supports. It has already been stated that a counterpoise, similar in every respect to the electrolysing tube, was used throughout the work. Consecutive weighings proved the adequacy of this procedure.

The Procedure.—A known amount of mercuric chloride* was placed on the cathode in the electrolysing tube with sufficient water to make a total volume of 25 or 30 cc., the sides of the tube having been carefully washed down. A few drops of a dilute solution of re-distilled hydrochloric acid were added to make the solution approximately one-fortieth normal. This was necessary to increase the conductivity of the solution at the outset, and this particular compound was chosen in order not to introduce ions other than those which would be present later. The water added was not sufficient to entirely dissolve the salt, so that the latter was dissolved, except in so far as its solubility was affected by the presence of substances formed during the course of the process, only as the solution became depleted by the electrolysis. With the strength of current used, the action had ordinarily proceeded for eight or ten hours before the disappearance of the solid phase. At the end of a similar period, the action was complete, as shown by the preliminary work, but traces of mercury compounds were probably adhering to the sides of the tube, and to the funnel placed in the mouth of the tube to prevent loss in the form of spray. An addition of approximately 20 cc. of water was made in washing the funnel and walls of the tube, and the current was allowed to pass several hours longer, after which no trace of mercury could be detected in the solution. Sometimes the whole process consumed forty-eight hours, varying altogether with the amount of salt to be electrolysed, and whether or not it was convenient to perform the subsequent operations. Copious fumes of chlorine escaped during the action, and as is usual in the electrolysis of mercuric chloride, insoluble particles said to be the mercurous compound gradually accumulated at the anode only to fall off and finally disappear. To prevent any of these particles from becoming permanently lodged between the glass surface and the cathode, the globule was agitated by a gentle whirling motion of the tube. This was not attempted, however, until the electrolysis was practically complete for fear of entangling solution, and



* From the *Journal of the American Chemical Society*, xxxii. No. 10.

* The non-hygroscopic character of the salt was proven in the previous work.

from that time on the process was repeated at intervals to ensure completeness. At no time was the agitation violent enough to sever the connection between the mercury and platinum. Sometimes the mercury exhibited a tendency to assume a form perhaps "deadened," and the separate particles had no tendency to unite with the main globule. Gentle tapping, however, generally sufficed to cause the formation of one globule. (In the preliminary experiments where less pure mercuric chloride was being dealt with, more difficulty was encountered). It is not unlikely that the disengagement of hydrogen from the cathode was the cause of the separation of these small particles.

To free the tube of conducting material at the end of the electrolysis, a funnel, with its stem almost reaching to the surface of the mercury, was placed in the tube, and without breaking the electric connections at least 500 cc. of pure water were poured into the tube, the overflow being caught in a large porcelain dish where any particles of escaping mercury could be detected. During the washing process, the tube was rotated as previously described, so that no chlorine would be retained between the cathode and glass, and thus remain in contact with the mercury after the breaking of the circuit. After removing the funnel, the water in the tube was decanted, the mercury with perhaps a drop or so of water remaining in the tube, owing to the bulb arrangement. Five washings were made with re-distilled acetone, each being decanted in turn. The tube was next immersed to its neck in a bath of acetone to free the outer surface of water, and was finally hung on a glass rod to dry. The counterpoise was subjected to exactly the same treatment. The two tubes hung side by side, and were gently agitated from time to time to prevent the possibility of the retention of any acetone between the globule and glass. Meanwhile, a current of air of the same intensity was passed over each globule, so that in a short time the vapour of acetone was effectually removed, and the tubes were full of air ready for their transfer to the balance arms. As soon as constant temperature was attained, the weighing was made by the method described before. Repetition of the drying process ensured its completeness.

The Results.

Preliminary Experiments.

No. of expt.	Sample of $HgCl_2$.	Weight of $HgCl_2$ in vacuum.	Weight of Hg in vacuum.	Atomic weight of mercury. (*a*)
1.	0	10·05743	7·43123	200·68
2.	0	8·41289	6·21687	200·71
3. (*b*)	0	10·99056	8·11897	200·52
4.	0	10·28282	7·59681	200·58
5.	0	19·57120	14·46032	200·65
			Mean	200·63

Final Experiments.

No. of expt.	Sample of $HgCl_2$.	Weight of $HgCl_2$ in vacuum.	Weight of Hg in vacuum.	Per cent Hg in $HgCl_2$.	Atomic weight of mercury. (*c*)
1.	2	8·14695	6·01909	73·882	200·61
2.	1	11·03881	8·15592	73·884	200·64
3.	1	13·48192	9·96129	73·886	200·66
4.	3	11·08026	8·18610	73·880	200·60
5.	3	11·31231	8·35819	73·886	200·66
6.	3	21·44026	15·84060	73·882	200·62
				73·883	200·63

(*a*) Calculated on the assumption that chlorine has the value 35·46 (*Journ. Am. Chem. Soc.*, xxxii., 4).

(*b*) In Experiment 3, a portion of the mercury became detached, and during the washing was poured into the catch dish. It is possible that the low value obtained in this case may be explained by the incomplete recovery of the separated particles.

(*c*) In the calculations, the atomic weight of chlorine has been taken as 35·46 (*Journ. Am. Chem. Soc.*, xxxii., 4).

The current was supplied by three storage cells, and was reduced by means of a suitable resistance to one- or two-tenths of an ampère. The action proceeded quietly, no spray being noticeable, and no rise of temperature above 30° took place.

It now remains to consider the results in this and in the previous paper:—

Series.		At. wt.
1.	The ratio $HgCl_2$: Hg (from the previous paper)	200·48
2.	The ratio $HgCl_2$: 2AgCl (from the previous paper)	200·62
3.	The ratio $HgCl_2$: Hg (preliminary experiments, this paper)	200·63
4.	The ratio $HgCl_2$: Hg (final experiments, this paper)	200·63

Giving each series equal weight, the mean value of the atomic weight of mercury becomes 200·59. It is reasonable, however, in seeking an optimum result to reject any series known to be faulty either on account of the nature of the material dealt with or in method. For the last reason, Series 1 is dropped, and for the first, Series 3 is thrown out. Considerable weight is attached to the mean value, 200·63, of the two remaining series for (1) the mercuric chloride analysed was the same in each, and, from the manner of preparation, it must have been practically free from foreign material, and (2) the complete analysis, by methods which seem above question, and which are radically different, shows that the sum of the mercury and chlorine contents gives essentially the real value. Thus:—

Per Cent Mercury.

From the fact that 56·52119 grms. of mercury resulted from 76·50051 grms. of mercuric chloride (Series 4)	73·883

Per cent Chlorine.

On the basis that 86·21813 grms. of silver were obtained from 81·66510 grms. of mercuric chloride (Series 2)	26·118
The sum	100·001

METALLIC STRONTIUM.*

By BEN L. GLASCOCK.

In no case has strontium been obtained in sufficient amount to admit of a thorough study of its properties. The most complete investigation thus far has been that of Guntz and Roederer (*Comptes Rendus*, cxliii., 400), who prepared the metal from its hydride, made from the amalgam.

The purpose of the present investigation was to develop, if possible, a process or method by which the metal could be obtained in sufficiently large quantities to continue the study of its properties. The electrolysis of the fused chloride offered the most promising solution. It had been shown conclusively by Bunsen and Matthiessen and by Stockem and Borchers that the metal could be made in this way (Borchers, *Elect. Metallurgie*, p. 84). The problem resolved itself, then, into devising an improved or simpler form of apparatus, or a change in the electrical conditions.

The objection to the method of Bunsen and Matthiessen is that with external heat (*Journ. Prakt. Chem.*, 1869, cvii., 253), in addition to that afforded by the passage of the current, it is exceedingly difficult to regulate the temperature of the furnace so that a crust of chilled strontium chloride will always cover the bath in the inner cell. Stockem and Borchers avoided this difficulty by collecting the metal at the bottom of the bath. They found that the metal did not combine with the strontium chloride to such

* From the author's Doctoral Thesis, 1909.

an extent as to render their method a failure. They cooled the bottom of the furnace, however, by means of a water jacket. The furnace of these workers is complicated, necessitating, as it does, the use of heavy insulation between the poles, a threaded point or rod for the cathode, and a water jacket for cooling purposes, all of which rendered the apparatus difficult of construction.

The method of Goodwin for the preparation of calcium suggested itself as a possibility for strontium (*Journ. Am. Chem. Soc.*, xxvii., 1403). To test it, a furnace was constructed by firmly binding together four Acheson graphite blocks by means of four heavy iron straps and bolts. The dimensions of the blocks were 10 cm. × 10 cm. × 30 cm. The two upper blocks had two semicircular sections sawed from them in such a way and of such a size that when they were fitted together they formed two holes 10 cm. deep, one 7·5 cm. in diameter, the other 10 cm. These holes fitted directly over depressions in the lower set of blocks, made by chipping out the graphite. Asbestos paper was put in between the blocks and the whole tightly bound together by means of the straps and bolts. The use of the asbestos was to prevent leaks, not to serve as insulation. The furnace was then connected to the + terminal of the feed wires by means of one of the bolts; thus all four blocks were connected with the current. An iron rod 2 cm. in diameter attached to the ratchet device used in the Goodwin furnace and connected to the − terminal served as the cathode. The circuit carried a 500-ampère ammeter and a 110-volt voltmeter, and a wooden barrel rheostat. The electrodes in the barrel were ordinary slabs of scrap iron, one of which could be lowered or raised by means of a cord passing over a pulley. If such a furnace would serve for the preparation of calcium it would be an improvement over the more or less fragile and complicated furnace of Goodwin, in that it could be taken apart entirely and the chilled calcium chloride left after the run easily removed, and in that it would do away with the use of the water-cooling apparatus, the graphite blocks being massive enough to conduct the heat away as rapidly as the water coil would, and also in that it would do away with the "gravity" cell of his furnace.

To try out the furnace, one of the holes was filled with melted calcium chloride, which had been fused in an iron dish in a wind furnace, the cathode lowered into the bath and the current switched on. Metallic calcium began at once to form on the iron, and rods of the metal as much as 20 inches in length were easily drawn out by means of the ratchet device. Each of the holes or furnaces were tried repeatedly. Each gave the same satisfactory results —they had equal efficiency. By repeated trials with varying current it was found that about 80 ampères and 40—50 volts gave the best results with this apparatus. This, of course, is a matter that is entirely dependent upon the size and depth of the bath. The furnace, when full, contained enough calcium chloride to last six to eight hours with the above current, the yield in metal being in the neighbourhood of 300 grms. As the object of these experiments was merely to show whether or not the furnace could be used successfully for calcium, no careful measurements or weights were taken with a view of ascertaining the efficiency of the apparatus. No inconvenience whatever was caused by leakage. Occasionally, however, a superficial lining of calcium fluoride was put into the furnace as an additional safeguard.

The Preparation of Metallic Strontium.

The apparatus described above was used with strontium chloride as the electrolyte, but metallic strontium was never obtained. It was impossible to prevent its burning and its combination with the electrolyte. It would not adhere to the cathode and thus become protected by a layer of strontium chloride, as is calcium in its preparation from calcium chloride. This may be due partly to the fact that it is less stable in the air than calcium is, and partly to the higher temperature of the electrolyte.

A cathode 6 cm. in diameter was substituted for the smaller one, and the current was just sufficient to keep the electrolyte molten. A layer of strontium chloride mixed with a small amount of metal was found to cover the end of the iron. A considerable quantity of hydrogen was evolved when the mixture was thrown into water. Three trials were made with this cathode with the same result.

A very small cathode, about 0·3 cm. in diameter, was next tried. The possibilities it held were that the intense heat in the immediate vicinity of the cathode would cause the liberated metal to fuse into globules and float, permitting their removal. After electrolysing for four to five hours, with a current sufficient to keep the whole bath molten, the cathode was removed. No strontium was attached to it, nor were globules of the metal observed on the surface of the bath at any time during the operation. There seemed, however, to be less burning than usual. When the cold mass was broken open, it was found to be full of violet coloured spots or nodules. These nodules gave considerable hydrogen when thrown into water. The experiment was repeated several times, but the results were never different.

It was thought perhaps metal could be obtained if the temperature of the electrolyte were lowered. For this purpose baths of strontium chloride with varying amounts of strontium fluoride were used. The cathode was the same as that used for calcium—2 cm. in diameter. When an electrolyte of strontium chloride and 10—20 per cent of strontium fluoride with a current of 140—150 ampères and 20—30 volts was employed, globules of metal formed and floated about on the surface of the bath. Several of these were taken out, but they ignited at once, burning energetically with an intensely red flame. When the burning metal was thrown on the floor it broke into pieces and flew in all directions, tracing figures, as calcium or antimony does under similar conditions. When the cathode was removed, it was found to be covered with a layer of strontium chloride about 0·6 cm. in thickness, which contained so much metal that pieces of it glowed when struck violently with a hammer, and caused a brisk evolution of hydrogen when thrown into water. If a less powerful current was used, the metal burned as fast as it was formed, and if the current was allowed to fall after the metal began to separate, the globules were seen to glow and to gradually disappear.

When a bath of strontium chloride and about 50 per cent of strontium fluoride with a current of 125 ampères and 40 volts was employed, it was noticed that small glowing particles were distributed through the mass, and they seemed to fall slowly to the bottom. Upon removing the cold material from the furnace, a thin black layer covered the bottom of it. It contained considerable metal and carbide.

This observation led to the next logical step—a reversal of the poles. This was done by placing a strip of sheet iron between the upper and lower sets of carbon, thus forming, at once, the cathode and the bottom of the furnace. A thick piece of asbestos with a hole in it to fit the furnace was laid over the iron, and the whole apparatus bound together as before, after the upper set of blocks had been separated from the iron straps and bolts by thick pieces of asbestos. A carbon rod 2·5 cm. in diameter served as anode. In other words, the furnace of Stockem and Borchers had been arrived at, but in a much simplified form.

Using this furnace with the bath last described and a current of 20—30 ampères and 70 - 80 volts for three hours, a layer was formed on the cathode which contained considerable metal and carbide. The metal was not in globules. With a bath of strontium chloride and 25 per cent of strontium fluoride and a current of 50—60 ampères and 50—60 volts for four hours a layer was obtained next to the cathode, which, in places, contained so much metal that when it was scratched, the whole took on a metallic lustre. This, of course, soon disappeared because of the instability of the metal in air. It decomposed water energetically.

A bath consisting of strontium chloride and 10 per cent of strontium fluoride was next used. The current was passed for seven and a-half hours. About half the time it registered 150 ampères and 20 volts, the other half 60 ampères and 50 volts. (During this electrolysis the carbons of the furnace attained a red-heat throughout. This would indicate that a water jacket is entirely unnecessary, since the metal had been obtained under these conditions). When the cold mass was broken open, it showed globules of metallic strontium. Many of the pieces were as large as a pea. Fourteen grms. of the metal were separated. In addition to the metal several nodules of a brilliant yellow substance were found. This was very brittle, and was rather stable in the air; when put into water an energetic evolution of acetylene occurred.

The experiment was repeated, with like results.

An attempt was made to fuse together the pieces of metal that were too small to be separated mechanically. The residue was put into a 2·5 cm. gas pipe, capped at the ends, and placed in a vertical position in a wind furnace. The strontium alloyed with the iron and holes appeared in the cap and pipe, although the temperature was much below that of the melting-point of iron.

The preceding experiences having demonstrated that any contrivance for cooling the furnace was unnecessary, it was decided to resort to an even simpler form of apparatus. To this end a cast-iron vessel of hemispherical shape 25 cm. in diameter and walls 0·6 cm. in thickness was made to serve as a container. To keep the liberated metal from contact with the air, and also to carry out Stockem and Borcher's idea of a small cathode, an iron rod 1·8 cm. in diameter, bent at right angles about 2 inches from its lower end, and this end then hammered to a blunt point, was made to serve as the cathode. A carbon rod 2·5 cm. in diameter was used as anode. By this arrangement the current was made to pass entirely beneath the surface of the bath, since the vessel was deep enough to prevent the current passing to it and thence to the other electrode. It also admitted of the use of a porous cell arrangement—Bunsen and Matthiessen's idea.

The vessel was filled with fused strontium chloride, the current switched on, and a porous plate interposed. The same bath was used on three different days, connection being established by drawing an arc from the iron cathode upon the anode by means of a thin carbon rod held in the hand until the electrolyte was sufficiently fused to carry the current. During the electrolysis the bath in the vicinity of the cathode was always covered with a crust of chilled chloride. A very small amount of metal was seen to burn, but when the mass was broken up after the third day, only about 1 grm. of metal was found. (A very interesting observation was made at this point. When the residue was put into water, preparatory to recovering strontium chloride, a vigorous evolution of acetylene and ammonia took place. The odour of phenyl isocyanide was also detected. The greater portion of the carbon from the anode, however, remained as carbon when the residue was leached out with water).

In the next experiment the dish was made to serve both as container and cathode, the anode remaining the same. Pure strontium chloride was used as the electrolyte. A current of 75 ampères and 75 volts was passed for three and a-half hours. Fifteen grms. of metal were obtained. There was a noticeable decrease in the amount of carbide observed. The globules were larger than heretofore. The mass was re-fused and a current of 75 ampères and 75 volts passed for eight hours. Toward the end of the electrolysis, globules of metal were seen to come to the surface and float to the edge of the dish and either burn there or sink. Efforts to remove these globules were not very successful. When the bottom of the electrolyte was disturbed by scraping it with a rod, large pieces of metal would rise to the surface, showing the presence of considerable strontium.

It was thought that the metal could be made to run into one large piece, if the vessel and its contents were heated in a wind furnace. This was done. The strontium alloyed with the iron, however, produced a large hole in the bottom of the dish. The temperature was far below the melting-point of iron. The iron in the vicinity of the hole was very soft, almost plastic, at low red-heat. When cold it was hard and brittle, and had a different fracture from cast-iron. A small amount of hydrogen was given off when it was boiled with water. Some of the metal was thoroughly washed, dissolved in hydrochloric acid, the solution filtered from the insoluble matter, and sulphuric acid and alcohol added to the filtrate. A heavy precipitate formed at once. Enough strontium was present to give a dense precipitate with sulphuric acid even in the absence of alcohol.

An iron mortar 15 cm. in diameter at the top and 15 cm high, having a capacity of 1 litre, was substituted for the iron vessel just described. A current of 45 ampères and 75 volts for eight hours gave about 7 grms. of material, which contained enough metal to render it malleable. Repeated trials failed to give any better results. The vessel was too small.

Another cast-iron vessel of the same dimensions as the first one was procured. A carbon anode 8 cm. × 8 cm. was substituted for the smaller one. This large carbon permitted the use of a lower current density at the anode, thus reducing the temperature of the bath. With an electrolyte of pure strontium chloride and a current of 125 ampères and 40 volts for seven hours, 76 grms. of metallic strontium were obtained, giving a current efficiency of 5·3 per cent. One piece of the metal weighed 8 grms. and several as much as 3 grms. This was the best yield obtained, but 30 to 50 grms. were easily isolated by duplicating the above conditions. In all 360 grms. of metallic strontium were made with this apparatus, which is extremely simple and involves the use of no expensive material. It was found that passing the current longer than six to eight hours decreased the actual yield, the best percentage yield being when a current of 135 ampères and 35 volts was passed for only two hours, 29·5 grms. of metal were isolated, or a current efficiency of 6·7 per cent was attained.

Vessels and anodes of varying size and electrolytes of varying composition were tried out, but the conditions previously mentioned gave the best results.

The best method for separating the metal from the mixture consists in crushing it on an ordinary iron plate, then sieving out the metal.

Some very interesting phenomena and products revealed themselves during the process of recovering the strontium chloride from the melts. When the melt from the pure strontium chloride bath was extracted with water, there remained a residue which was soluble in hot water. Upon cooling this solution crystals separated. They had an alkaline reaction and all the properties of strontium hydroxide.

Upon concentrating the mother-liquor from these crystals it took on a pink colour, which grew more intense as the concentration proceeded. The solution was alkaline. On addition of acid the colour changed to light yellow. Bases restored the pink colour. This product was obtained repeatedly, but never in amounts large enough to permit of the determination of its constitution,

To remove the iron salts from the first water extract, containing most of the strontium chloride, the solution was evaporated to dryness with a small amount of nitric acid and then baked, the residue extracted with water, and the extract made ammoniacal. The ammonium hydroxide instead of giving a red-brown precipitate of ferric hydroxide gave a voluminous white precipitate that resembled aluminium hydroxide. Examination showed that it was neither an aluminium nor a titanium compound.

When the solution was evaporated to dryness without the addition of nitric acid, a blue tint would often appear around the edges of the residue, suggesting the presence of cyanide in the solution.

Properties of Metallic Strontium.

Strontium is a very light soft metal of a silver lustre when a new surface is first exposed; this, however, rapidly changes to a yellowish tint, and finally to a white non-lustrous surface as the layer of oxide forms over it. It is harder than sodium but softer than calcium; it can be cut easily with a knife. It reacts with water, with methyl and ethyl alcohols, acetoacetic and malonic esters, and aniline with the evolution of hydrogen. It reacts slowly with ethyl iodine at the boiling-point of the latter. It has no action upon silicon tetrachloride in either the hot or cold condition. It alloys with iron, and seems to combine with amorphous chromium and boron when heated with them. It dissolves very easily in liquid ammonia, giving a deep blue solution from which a dark blue precipitate separates as more metal dissolves. As the ammonia evaporates from this precipitate it passes through the beautiful play of colours that a clean sheet of copper shows as it cools after being heated to a high temperature, finally exhibiting a bright bronze lustre and passing into a white compound as all the ammonia evaporates. Strontium burns in an atmosphere of carbon dioxide and illuminating gas as energetically as it does in air, but not so violently as calcium does under similar conditions. Carbon is set free and some carbide is formed when it burns in the former. Hydrogen and nitrogen unite with the heated metal when they are passed over it, forming the hydride and nitride respectively. The hydride reacts more energetically with water and alcohol than the metal does.

On analysis three different samples of the metal gave the following results :—

	I.	II.	III.
Insoluble	0·04	0·04 | 0·02	0·92
$Fe_2O_3(Al_2O_3)$ ..	0·14		
Sr	97·11	98·50	98·54
Ca	—	—	None
Mg	—	—	None
Cl	1·75	—	—
O (by difference)	0·96	—	—
	100·00		

The specific gravity of strontium determined in dry toluene in a 50 cc. pyknometer gave the value 2·55.

The specific heat of the metal, determined in an ordinary water calorimeter, by putting a weighed amount of the metal into an ordinary test-tube, covering it with a weighed quantity of dry toluene, and then the tube sealed off as near the surface of the liquid as possible, gave the following results after corrections had been made for the toluene and glass by means of a blank :—

	0·0779
	0·0701
	0·0736
	0·0757
	0·0771
	0·0681
	0·0768
Average ..	0·0742

This value multiplied by the atomic weight of strontium give 6·5 as Dulong and Petit's constant.

Alloys.

Various alloys of strontium have been described. Willner ("Dissertation," Freidrich Wilhelm Universität, Z. Berlin, 1907) has made and analysed alloys of strontium with tin, magnesium, and aluminium.

An alloy of iron and strontium has not been mentioned in the literature. Such an alloy made in an accidental way has been noted in the first part of this communication. Hirsch and Aston have shown that pressure is necessary for the alloying of calcium and iron (*Proc. Am. Electrochem. Soc.*, xiii., 143). It was thought that strontium and iron would unite at atmospheric pressure. To test this assumption some iron, reduced by hydrogen (90 per cent), was put into a hard glass tube, a few pieces of strontium placed on top of it, and the whole covered with iron. The tube was drawn down to a capillary and then sealed off, when the end containing the mixture was heated to low redness. It was then heated in a good blast-lamp. When the fusion point of glass was reached the sides of the tube just above the iron fell inward; heat was applied until the glass began to be blown outward. When a bright red heat was reached, portions of the contents were seen to glow. Upon breaking open the tube, a lump of rather hard metallic alloy was found inside. On filing, it presented a bright homogeneous metallic surface; the lustre soon disappeared, however. The alloy decomposed water readily. On analysis it gave :—

	Per cent.
Insoluble	0·32
Iron	70·14
Strontium	22·95

An alloy was made by fusing iron by hydrogen in the electric furnace and then plunging strontium into the molten mass. A better one, however, was obtained, by plunging the metal into molten cast-iron. Each slowly evolved hydrogen from water.—*Journal of the American Chemical Society*, xxxii., No. 10.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

The Council has ordered the following letter and report to be printed in the *Journal* and *Proceedings* of the Society :—

Imperial College of Science and Technology,
South Kensington, London, S.W.,
August 22nd, 1910.

Gentlemen,—I beg to forward the Annual Report of the International Committee on Atomic Weights for 1911, to which I have appended, by their desire, the signatures of Professors Ostwald and Urbain.

The Committee, it will be seen, have acceded to the wish of the Council of the Chemical Society, and have prepared the Report in such time that it can be published prior to the commencement of the ensuing academic year.

Slight changes have been made in the atomic weights of argon, helium, krypton, lithium, neon, phosphorus, platinum, strontium, vanadium, and xenon, but otherwise the new table remains very much as in 1910.—I have the honour to be, Gentlemen, your obedient servant,

T. E. Thorpe.

To the Hon. Secretaries,
The Chemical Society.

(The Report was inserted in the Chemical News, vol. cii., p. 199).

The following are abstracts of papers received during the vacation, and published or passed for publication in the *Transactions* :—

200. "Δ^3-p-*Menthenol*(8) *and* Δ-3 : 8(9)-p-*Menthadiene*." By William Henry Perkin, Jun., and Otto Wallach. (*Trans.*, 1910, 1427).

The authors have prepared the above substances and several of their derivatives from two sources, namely, from 1-methyl-Δ^3-*cyclo*hexene-4-carboxylic acid and from 4-acetyl-1-methyl-Δ^3-*cyclo*hexene :—

$$CHMe<\begin{matrix}CH_2—CH\\CH_2.CH_2\end{matrix}>C\cdot CO_2H \rightarrow$$

$$CHMe<\begin{matrix}CH_2—CH\\CH_2.CH_2\end{matrix}>C\cdot COMe \rightarrow$$

$$CHMe<\begin{matrix}CH_2—CH\\CH_2.CH_2\end{matrix}>C\cdot CMe_2\cdot OH,$$

and they give a careful comparison of the physical properties of these substances with those of terpineol, limonene, and their corresponding derivatives.

201. "*Freezing-point Curve for Mixtures of Camphor and Phenol.*" By John Kerfoot Wood and Janet Drummond Scott. (*Trans.*, 1910, 1573).

The authors have determined the freezing-points of a large number of mixtures of camphor and phenol, ranging n composition from pure phenol on the one hand to pure camphor on the other. The form of the freezing-point curve indicates the formation of a compound, the freezing-point of which is - 18·6°, between equimolecula proportions of camphor and phenol. The curve also shows that eutectic mixtures are produced when the molecula. percentage of camphor in the mixture amounts to either 29·5 or 59·21; in the former case the eutectic mixture is composed of phenol and the compound, and in the latter case of camphor and the compound. The freezing-points of the two eutectic mixtures are respectively −30·5° and −32·0°.

No evidence was obtained by the authors as to the existence of the hemi-camphoride of phenol mentioned by Léger (*Comptes Rendus*, 1890, cxi., 109).

202. "*The Absorption Spectra of Aniline and its Homologues as Vapours, as Liquids, and in Solution.*" By John Edward Purvis. (*Trans.*, 1910, 1546).

The results of this investigation show that—(1) the vapour of aniline has a considerable number of absorption bands, which show relationships amongst themselves both in structure and in differences of wave-lengths; (2) the vapours of the homologues of aniline show none of these absorption bands; (3) the solutions in alcohol show absorption bands in all the substances, and the type and position of the bands are regulated by the replacement, by alkyl groups, of the hydrogen in the amino-group or in the nucleus; (4) none of the substances in the liquid condition exhibit absorption bands through the thinnest films of 0·001 mm. thick. The phenomena are discussed from a consideration of the vibrations of symmetrically and unsymmetrically oriented molecules in different physical conditions.

203. "*Condensations of Phenanthraquinone with Ethyl Malonate and Ethyl Acetoacetate.*" By Marion Brock Richards. (*Trans.*, 1910, 1456).

Japp and Wood (*Trans.*, 1905, lxxxvii., 712) described some condensations of phenanthraquinone with ketonic compounds under the influence of acetic anhydride containing a little concentrated sulphuric acid.

The condensation products of phenanthraquinone with ethyl malonate and with ethyl acetoacetate, of which mention was made in that paper, have now been further investigated.

In the case of the ethyl malonate reaction, two compounds were obtained, namely, *ethyl phenanthroxylacetoxymalonate*, $C_{23}H_{22}O_7$ (m. p. 109·5°) and *ethyl 2-keto-3-acetoxy-4 : 5-diphenylene-2 : 3-dihydrofuran-3-carboxylate*, $C_{21}H_{16}O_6$ (m. p. 163·5°), and it was found that the former could be transformed into the latter compound by further action of the reagent. Reduction of the second compound with hydriodic acid yielded *2-keto-4 : 5-diphenylene-2 : 3-dihydrofuran*, $C_{16}H_{10}O_2$ (m. p. 177°), from which the corresponding acid, *9-hydroxy-10-phenanthrylacetic acid*, $C_{16}H_{12}O_3$ (m. p. 182—183°), was also prepared.

The ethyl acetoacetate reaction also gave two compounds, namely, *ethyl 9-phenanthroxylacetoxyacetoacetate*, $C_{22}H_{20}O_6$ (m. p. 148°), and a *substance*, $C_{22}H_{18}O_5$ (m. p. above 315°), and, again, further action of the reagent caused the first substance to be transformed into the second.

204. "*The Constitution and Mutarotation of Sugar Anilides.*" By James Colquhoun Irvine and David McNicoll. (*Trans.*, 1910, 1449).

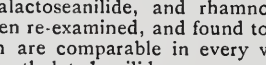
The anilides of tetramethyl mannose, tetramethyl galactose, and trimethyl rhamnose have each been obtained crystalline in mutarotatory forms. The compounds are recovered unchanged after treatment with silver oxide and methyl iodide, and are thus to be regarded as derivatives of the γ-oxidic forms of the parent sugars.

As the anilides of the corresponding unsubstituted sugars are very readily hydrolysed, the method of determining their constitution by the results of alkylation (*Trans.*, 1908, xciii., 1429) cannot be applied, but their structural resemblance to the methylated γ-oxidic anilides is shown in the mutarotation exhibited by the compounds. Mannoseanilide, galactoseanilide, and rhamnoseanilide have accordingly been re-examined, and found to display optical changes which are comparable in every way with those shown by the methylated anilides.

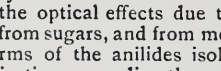
Comparison of the optical effects due to glucoside and anilide formation, from sugars, and from methylated sugars, shows that the forms of the anilides isolated in the pure state by crystallisation are directly comparable with β-glucosides.

205. "*Cyclic Di- and Tri-ketones.*" By Siegfried Ruhemann. (*Trans.*, 1910, 1438).

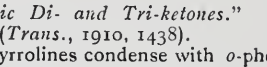
The diketopyrrolines condense with *o*-phenylenediamine with the production of phenazines. Diketodiphenylpyrroline and diketophenyl-*p*-tolylpyrroline, respectively, yield thus:—*Diphenylpyrrolinophenazine*,—



or its homologue. These compounds, like all other members of this group, are yellow, but the condensation products, $C_{20}H_{16}ON_2$, which is formed from *o*-phenylenediamine and diketoacetylphenylmethyl*cyclo*pentene,—



is purple. This fact indicates that the substance $C_{20}H_{16}ON_2$ has not the constitution of the phenazines, but—



and that its formation is preceded by the change of the diketo*cyclo*pentene derivative, $C_{14}H_{12}O_3$, into its tautomeric form, which exists, also, in the blue salts of this diketone (see *Trans.*, 1909, xcv., 984).

With the view of preparing 1 : 2-diketohydrindene, $C_6H_4<\begin{matrix}CO—\\CH_2\end{matrix}>CO$, the author studied the action of *p*-nitrosodimethylaniline on α-hydrindone, -

$$C_6H_4<\begin{matrix}CO—\\CH_2\end{matrix}>CH_2,$$

and found that the nitroso-compound attacks both CH_2 groups of the hydrindone. The green condensation product, $C_{25}H_{26}O_2N_4$, which is formed, is decomposed by dilute sulphuric acid, and yields the colourless *hydrate* of *triketohydrindene*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C(OH)_2$. Its physical properties and some of its interesting reactions are described.

206. "*The Relation between Solubility and the Physical State of the Solvent in the case of the Absorption of Carbon Dioxide in p-Azoxyphenetole.*" By Ida Frances Homfray. (*Trans.*, 1910, 1669).

A homogeneous solution phase, in the normal liquid or gaseous states, may be present in equilibrium with practically all solids, liquids, or gases in other co-existing phases. In the case of mixtures in the so-called solid state, however, a distinction must be drawn between the crystalline and the amorphous forms. The term solid should, strictly speaking, be confined to the former, the latter having rather the properties of a highly super-cooled fluid. All available evidence appears to show that the directive forces of crystallisation almost entirely prevent molecular interpenetration. *p*-Azoxyphenetole is a crystalline substance, which melts at 138° to a crystalline liquid, changing at 165° to an isotropic normal liquid. The absorption of carbon dioxide

in these phases has been determined in a specially constructed apparatus, unabsorbed gaseous volumes being measured. It was found that no absorption takes place in the solid crystalline phase. After the first melting-point, some absorption occurs. On further raising the temperature, thermal expansion continues until the clearing point is reached. Then, however, a second maximum volume is passed through, a very considerable increase of absorption occurring. After equilibrium has again been established, thermal expansion and decrease of solubility proceed regularly. On reversing the process, the same maximum and minimum readings are repeated.

The remarkable result is thus obtained that, in spite of the lower temperature of the crystalline liquid phase, its solvent power is much smaller than that of the isotropic phase, whilst solution or adsorption in the solid phase is entirely absent.

207. "*The Triazo-group.* Part XIV. *Azoimides of the Acetoacetic Series.*" By Martin Onslow Forster and Sidney Herbert Newman. (*Trans.*, 1910, 1360).

For the purpose of comparison with azoimides of the malonic series, *methyl* and *ethyl α-triazomethylacetoacetates*, *ethyl α-triazoethylacetoacetate*, and *ethyl αα-bistriazoacetoacetate* were prepared by interaction of the corresponding chloro-derivatives and sodium azide. In each case the triazo-ester was obtained with much greater difficulty than was presented by the triazomalonic esters.

Ethyl *α*-triazomethylacetoacetate is transformed by ammonia into *α*-triazopropionamide, whilst hydrochloric acid resolves it into diacetyl.

208. "*Optically Active Methoxysuccinic Acid from Malic Acid.*" By Thomas Purdie and George Ballingall Neave. (*Trans.*, 1910, 1517).

The authors have prepared the methyl, ethyl, and propyl esters of *l*-methoxysuccinic acid by methylating malic esters with methyl iodide and silver oxide with the object of controlling and extending the polarimetric observations formerly made (*Trans.*, 1893, lxiii., 217, and succeeding papers), on the same compounds, obtained by resolution of inactive methoxysuccinic acid with the aid of alkaloids. The values of the rotatory powers of the esters and acid from the two different sources are in fair agreement.

The optical relationships of the ethereal *l*-methoxysuccinates with the *d*-dimethoxysuccinates (*Trans.*, 1901, lxxix., 963), in the pure liquid state and in solution, are pointed out, also the relationships of these esters with the parent malates and tartrates.

The diamide and dianilide of *l*-methoxysuccinic acid were prepared, and their rotatory powers in solution compared with those of maldiamide and maldianilide in similar solvents.

209. "*Optically Active Derivatives of* l-*Methoxy- and* d-*Dimethoxysuccinic Acids.*" By Thomas Purdie and Charles Robert Young. (*Trans.*, 1910, 1524).

The authors have prepared further derivatives of these acids, including the anhydrides and dichlorides. Polarimetric examination of the latter afforded no evidence that they were mixtures of two tautomeric forms of the type frequently assigned to succinyl chloride. The molecular rotations of *l*-methoxysuccinic acid and a number of its derivatives approximate to the halved values of the corresponding dimethoxy-compounds. It is pointed out that the movements of rotation attending the conversion of alkyloxy-, acyloxy-, and halogen-succinic acids of *d*- and *l*-configuration into chloride, ester, and anhydride are always in the dextro- and lævo-direction respectively, irrespective of the sign of rotation of the initial acid.

The action of sodium methoxide on methyl *l*-methoxysuccinate gave an optically inactive condensation compound, apparently identical with a substance obtained similarly (*Trans.*, 1891, lix., 472) from methyl fumarate. The products of the action of magnesium methyl iodide and of magnesium phenyl bromide on methyl *d*-dimethoxysuccinate were *γδ-dimethoxy-βε-dimethylhexane-βε-diol* (m. p. 71°) and 3 : 4-*dimethoxy*-2 : 2 : 5 : 5-*tetraphenyltetrahydrofuran* (m. p. 185°) respectively; both compounds are lævorotatory.

210. "*Action of Grignard Reagents on Methyl* l-*Methoxysuccinate, Methyl Maleate, and Maleic Anhydride.*" By Thomas Purdie and Paul Seidelin Arup. (*Trans.*, 1910, 1537).

The action of magnesium methyl iodide on methyl *l*-methoxysuccinate is similar to that of the same reagent on the *d*-dimethoxy-ester previously described, the product being optically active *γ*-methoxy-*βε*-dimethylhexane-*βε*-diol. Dehydration, however, occurred in the course of isolating the compound by distillation, and the final product obtained was the oxide of the glycol, or possibly an isomeric unsaturated alcohol. The substance is dextrorotatory.

Two crystalline compounds were isolated from the product of the action of magnesium phenyl bromide on methyl *l*-methoxysuccinate, namely 2 : 2 : 5 : 5-*tetraphenyl*-2 : 5-*dihydrofuran* (m. p. 190—191°) and a *triphenylbutyrolactone* (m. p. 160—161°), both optically inactive. The latter compound, on being heated with mineral acids, was converted into an isomeric lactone (m. p. 197°). With the view of elucidating the reactions concerned in the production of these compounds, the authors examined the action of magnesium phenyl bromide on methyl fumarate and maleate, and on maleic anhydride. The product in the case of methyl fumarate was an uncrystallisable oil from which no pure substance could be isolated. Methyl maleate gave the abovementioned dihydrofuran derivative, and maleic anhydride gave A. Smith's desylacetophenone (*Trans.*, 1890, lvii., 643).

211. "*The Intramolecular Re-arrangement of Diphenylamine Orthosulphoxides.* Part III. *The Tri- and Tetrachlorosulphoxides.*" By Oscar Lisle Brady and Samuel Smiles. (*Trans.*, 1910, 1559).

In a previous paper the mechanism of this re-arrangement was discussed, and the hypothesis was advanced that it depends on the preliminary formation of a salt of the sulphoxide. The tri- and tetrachloro-sulphoxides of diphenylamine have now been prepared by the action of hydrogen dioxide and hydrochloric acid on thiodiphenylamine, and these have been fully investigated with the object of isolating their salts. This has been accomplished in the case of the trichloro-derivative, the hydrochloride of which is readily converted into the azothionium compound by warming in certain media. It is considered that the explanation previously given to this reaction is thus confirmed.

212. "*The Rate of Hydration of Acid Anhydrides Succinic, Methylsuccinic, Itaconic, Maleic, Citraconic, and Phthalic.*" By Albert Cherbury David Rivett and Nevil Vincent Sidgwick. (*Trans.*, 1910, 1677).

The authors have investigated the rate of hydration of these anhydrides by means of the conductivity, by a method described for acetic anhydride in a previous paper (*Trans.*, 1910, xcvii., 732). In all cases the reaction was found to be unimolecular, and not to be catalysed by hydrogen ions. The slight variation of the rate with concentration previously found with acetic anhydride was not observed with any of these cyclic anhydrides, with the possible exception of methylsuccinic. The velocities are given in the table (the mean value for acetic anhydride being added for comparison), together with the dissociation constants of the corresponding acids.

It will be seen that succinic anhydride, with its saturated, five-membered ring, which on Baeyer's theory has practically no strain, is hydrated with almost the same velocity as the open-chain acetic anhydride. The velocity is greatly increased by a double link, less by a benzene link. With the exception of methylsuccinic anhydride, the order of the velocities is the same as that of the dissociation constants. The introduction of a methyl group raises the velocity of succinic anhydride and lowers that of maleic; it has the

same effect on the dissociation constants of the corresponding acids.

Anhydride.	Velocity constant.		Dissociation constant of acid.	
	Absolute.	Relative.	Absolute.	Relative.
[Acetic	0·001148	0·99]	—	—
Succinic	0·001155	**1·00**	0·0066	**1·00**
Methylsuccinic . ..	0·001609	1·39	0·0086	1·30
Itaconic (methylene-succinic)	0·001294	1·12	0·012	1·82
Maleic	0·0115	9·96	1·2	182
Citraconic (methyl-maleic)..	0·00765	6·62	0·34	51·5
Phthalic	0·00461	3·99	0·121	18·3

213. "*Ethyl 6-Methyl-2-pyrone-3 : 5-dicarboxylate and its Conversion into Methyltrimesic Acid.*" By JOHN LIONEL SIMONSEN. (*Trans.*, 1910, 1910).

Ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate (*Trans.*, 1908, xcviii., 1022), on hydrolysis, is converted into *methyltrimesic acid*, which on oxidation gives prehnitic acid. The condensation of ethyl propiolate and ethyl acetoacetate was also investigated.

214. "*The Action of Bases on αβ-Dibromobutyric Acid and its Esters.*" By THOMAS CAMPBELL JAMES. (*Trans.*, 1910, 1565).

The action of various alkalis, tertiary bases, and alkaloids in abstracting hydrogen bromide from *αβ*-dibromobutyric acid has been examined. The reaction of the acid with aqueous potassium hydroxide has been followed kinetically, and shown to be strictly bimolecular.

In the case of all the bases used, the products consists of a mixture of α-bromo- and α-bromo*allo*-crotonic acids, the proportion of the former being greater the weaker the base used.

When esters are used instead of the free acid, the proportion of α-bromo-acid is not increased to anything like the same degree as in the case of the analogous decomposition of *αβ*-dibromo-*β*-phenylpropionic acid (cinnamic acid dibromide).

215. "*The Absorption Spectra of Furan Furfuraldehyde, Thiophen, and Pyrrole under different Conditions.*" By JOHN EDWARD PURVIS. (*Trans.*, 1910, 1648).

The results of the investigation are :—1. The vapour of furan exhibits absorption bands, some of which are similar in appearance and have similar differences in wave-lengths ; the vapour of furfuraldehyde also exhibits bands which can be grouped together, but which are different from those of furan ; the vapours of thiophen and pyrrol show a few bands, two of which are comparable with two in the vapours of furan and of furfuraldehyde. 2. Alcoholic solutions of furan, thiophen, and pyrrole show no absorption bands, whilst a N/1000-solution of furfuraldehyde shows a strong band in the ultra-violet. 3. The liquids, furfuraldehyde, thiophen, and pyrrol, show no absorption bands.

216. "*The Viscosity of certain Amides.*" By ALBERT ERNEST DUNSTAN and ALBERT GEORGE MUSSELL. (*Trans.*, 1910, 1935).

The authors have determined the viscosities of a considerable number of amides in the free state in aqueous solution and in pyridine solution. They find that in aqueous solution the simple fatty amides are still associated to a considerable extent, and that formamide is largely dissociated. The amides in the fused condition are associated, but whilst acetanilide has a high molecular viscosity, pointing to great association, methylacetanilide exists in a much more simple molecular condition. In pyridine solution the amides show little signs of the acidic character which would be expected did they possess the hydroxyiminic structure. With the exceptions of thiocarbamide, diphenylthiocarbamide, and cyanuric acid, the molecular viscosities are normal.

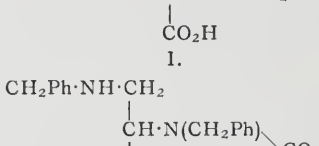
217. "*Changes in Volume in the Formation of Dilute Solutions.* Part II. *Relationship between Change in Volume and Constitution.*" By HARRY MEDFORTH DAWSON. (*Trans.*, 1910, 1896).

It is shown that the change in volume which accompanies the formation of dilute solutions of a given substance in a series of solvents is determined by the internal pressures, and the compressibilities of the solvents provided that the formation of the solution is unaccompanied by changes in the degree of complexity of the solute and solvent, and that the two kinds of molecules do not enter into combination. Such solutions are termed "normal" solutions. Experimental observations relating to iodine solutions indicate that combination between iodine and the solvent is of frequent occurrence. Since this combination is accompanied by an alteration in volume, the observed changes in volume in the formation of iodine solutions are not, as a rule, in agreement with the requirements of the equation deduced for "normal solutions." In some few cases, however, the relative volume changes are such as are anticipated by theory.

The absence of parallelism in the volume changes when two substances are dissolved in the same series of solvents is also consistent with the view that solvates are usually formed in dilute solutions.

218. "*αβ-Dibenzylaminopropionic Acid and 1 : 7-Dibenzyltetrahydrouric Acid.*" By EDWARD PERCY FRANKLAND. (*Trans.*, 1910, 1686).

Following the method adopted by the author in the recent synthesis of tetrahydrouric acid, a dibenzyltetrahydrouric acid was prepared by the action of cyanic acid on *αβ-dibenzylaminopropionic* acid (I.), one of the carbamide groups being condensed with the carboxyl group by means of 25 per cent hydrochloric acid :—



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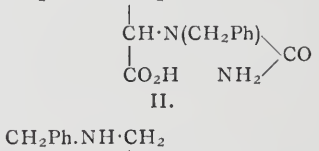

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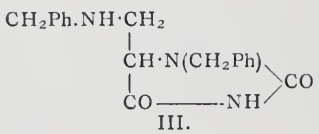

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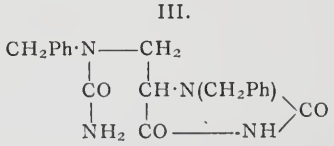


IV.

The first product of the action of cyanic acid on the dibenzylaminopropionic acid was probably *β-benzylamino-α-benzylcarbamidopropionic acid* (II.) (m. p. 200—201°), which was condensed with hydrochloric acid to *β-benzyl-γ-benzylaminomethylhydantoin* (III.) (m. p. 112—115°). One of the benzylamino-groups remained unacted on, and was capable of salt formation with a molecule of hydrochloric acid. The free base was converted into 1 : 7-*dibenzyltetrahydrouric acid* (IV.) by prolonged heating with an excess of potassium cyanate in aqueous methyl alcohol ; it forms prismatic crystals, melting with slight decomposition at 177—178° (uncorr.).

The *αδ*-dibenzylaminopropionic acid was obtained by boiling a solution of benzylamine in chloroform with *αβ*-dibromopropionic acid. The free dibenzylamino-acid is sparingly soluble in water with an alkaline reaction to litmus ; it forms rhomboidal plates, melting and decomposing at 181—184° (uncorr.).

219. "*Contributions to the Chemistry of the Terpenes.* Part VII. *Synthesis of a Monocyclic Terpene from Thymol.*" By George Gerald Henderson and Maggie Millen Jeffs Sutherland. (*Trans.*, 1910, 1616).

From thymol, $C_6H_3MePr\beta\cdot OH$, the authors prepared thymoquinone, which, on reduction with sulphuric acid, yielded thymoquinol, $C_6H_2MePr\beta(OH)_2$. This dihydric phenol, when heated with hydrogen in presence of nickel according to the method of Sabatier and Senderens, was converted into the saturated disecondary alcohol *menthane-2 : 5-diol*, $C_{10}H_{18}(OH)_2$. This compound forms very small colourless crystals. It melts at 112°, and boils at about 155°/15 mm. It is very readily soluble in alcohol, ether, or light petroleum, readily so in benzene, and very sparingly so in water. When heated at 110—200° with anhydrous potassium hydrogen sulphate, it yields a *terpene*, $C_{10}H_{16}$, which is a colourless liquid, boiling at 179°/760 mm. It has a rather faint odour somewhat like that of limonene, and is practically insoluble in water, but readily soluble in the usual organic solvents. It at once reduces permanganate, and unites additively with bromine, but apparently does not react with nitrous acid to form a nitrosite. It is probably $\Delta^{1:4}$-menthadiene, $\begin{matrix} CMe{:}CH\cdot CH_2 \\ | \quad\quad | \\ CH_2\cdot CH{:}C\cdot CHMe_2 \end{matrix}$.

220. "*Contributions to the Chemistry of the Terpenes.* Part VIII. *Dihydrocamphene and Dihydrobornylene.*" By George Gerald Henderson and Ernest Ferguson Pollock. (*Trans.*, 1910, 1620).

When heated with hydrogen in presence of nickel according to the method of Sabatier and Senderens, bornylene, $C_{10}H_{16}$, is easily converted into *dihydrobornylene*, $C_{10}H_{18}$, which appears to be identical with the saturated hydrocarbon camphane. When camphene, $C_{10}H_{16}$, is hydrogenated in a similar manner, the reaction is not so complete, and the nature of the product depends on the temperature. At 120—180° a solid product melting at about 64°, was obtained, which by fractional crystallisation from methyl alcohol was proved to be a mixture of dihydrocamphene, $C_{10}H_{18}$, already prepared by Vavon (*Comptes Rendus*, 1909, cxlix., 997) with a small proportion of unchanged camphene. At a higher temperature a liquid was produced, which was also found to be a mixture, containing dihydrocamphene, a little unchanged camphene, and a small proportion of a third substance which was not further investigated. Dihydrocamphene, unlike dihydrobornylene, differs widely from camphane in melting-point and other physical properties.

These results confirm the view that the arrangement of the carbon atoms in the molecule of bornylene is the same as in that of camphane, and that the structure of the molecule of camphene is of a different type.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, October 28, 1910.

Prof. H. L. Callendar, F.R.S., President, in the Chair.

A paper entitled "*A New Method for producing High Tension Discharges*" was read by Prof. Ernest Wilson and Mr. W. H. Wilson.

According to this method energy is taken from an alternating or continuous current source, and stored in a magnetic field by an inductance ; it is then permitted to surge into a condenser which forms with the inductance a *low* frequency oscillating circuit. When the energy is stored in the condenser the latter is mechanically bridged across the primary winding of a spark-coil, with which it forms a *high* frequency oscillatory circuit. The energy is then transmitted by the secondary winding of the spark-coil to the work circuit in well known manner.

The method therefore involves the use of an inductance, a condenser, a spark-coil, and a special contact-making device. In one form, the contact-maker consists of a cylinder of insulating material driven by a small motor, the cylinder carrying a metal segment, and a complete ring of metal attached to the segment. Three brushes (Nos. 1, 2, 3) bear upon the cylinder. No. 1 makes contact with the segment once in a revolution, No. 2 is continuously in contact with the ring, and No. 3 makes contact with the segment once in a revolution, and is mounted on an adjustable arm. According to one method of connection, the coil of the inductance is connected in series with the primary winding of the spark-coil, and forms one circuit. In parallel with this circuit is placed the condenser. One pole of the supply source is connected to brush No. 1 on the contact-maker. The other pole of supply is connected to a tapping point on the inductance suitable for the voltage of supply, the total number of turns on the inductance depending upon the voltage at which it is desired to charge the condenser. The junction of the inductance and the condenser is connected to brush No. 2 on the contact-maker, and is therefore continuously in contact with the metallic segment. The junction of the inductance and the primary winding or the spark-coil is connected to brush No. 3, which is capable of adjustment.

At the epoch of "make," brushes Nos. 1 and 2 are connected by the segment, and the system is switched on to the supply source. The current rises in the winding of the inductance and builds up the magnetic field. The condenser also becomes charged, and its charging current passes through the primary winding of the spark-coil. At the period of "break," brush No. 1 severs contact with the segment, and is insulated. The energy stored in the condenser is added to that in the inductance, and the condenser begins to be charged in the reverse direction. Ultimately the whole energy in the system is stored in the condenser. Brush No. 3 is so adjusted that, at this moment, it begins to touch the segments of the contact-maker, and thereby short-circuits the inductance. The condenser then discharges with great rapidity through the primary winding of the spark-coil, and the energy oscillates to and fro. As is well known, the electromotive force induced in the secondary winding may be of an oscillatory or uni-directional character according to the nature of the work circuit. As only the current in the condenser passes through the primary winding of the spark-coil at "make," the inverse electromotive force induced in the secondary winding is so small as to be negligible, but if desired it can be entirely eliminated by a modification in the connections.

Briefly the following are some of the advantages gained :—

1. For X-ray work the inverse electromotive force at "make" is eliminated, thereby leading to increased life of the tube and to a more sharply defined radiograph.

2. Only a small magnetising current is required as the inductance has a nearly closed magnetic circuit. This gives rise to a very small C^2R loss, and consequently higher efficiency.

3. On account of the long periodic time of the system between the periods of "break" and "short-circuit," the voltage across the contact of the interrupter at "break" does not rise to a high value, or rises so slowly that the contacts are well separated before it is developed. Hence immunity from sparking.

4. The method lends itself to few secondary turns, and this keeps down the time constant. It also makes the coil lighter, cheaper, and more compact.

5. The method lends itself to low secondary resistance —a point of great importance in connection with radio-telegraphy.

6. The iron or the spark-coil can be kept small in amount, and special attention can be paid to its lamination and insulation, as it may have to be operated at frequencies of three or four thousand per second.

7. The elimination of sparking increases efficiency, and on board ship where coal-gas is not conveniently obtainable this is an advantage.

8. The apparatus can be worked from direct current or

alternating current systems at usual voltages, or from a portable battery of a few storage-cells.

9. The oscillatory current at "break" does not pass through the battery, and hence does not assist in its discharge.

10. The iron in the magnetic circuit of the external inductance has only to operate at low frequency, and hence it has not to be finely laminated.

11. When used on alternating current systems rectification, if desired, is easily effected by employing two short circuiting brushes, one for each half-period, and allowing the second brush to short-circuit at the moment when the condenser is fully charged after allowing a second complete surge of the energy between the condenser and the inductance of the spark-coil.

12. The apparatus is light, efficient, and cheap, and is suitable for radio-telegraphy, X-ray, medical, and other work in which high-tension electricity is employed.

The following are a few particulars of the apparatus exhibited at the meeting:—

Spark length of secondary winding ..	10 inches
Secondary turns	16,000 to 20,000
Primary turns	78
Secondary resistance (aluminium) . ..	2900 ohms.
Primary resistance	0·056 ohm.
Weight of spark-coil and condenser ..	10 lbs.
Weight of inductance and interrupter ..	20 lbs.

Mr. A. CAMPBELL asked if the adjustment of the commutator was made experimentally, and if the instrument could produce high frequency oscillations suitable for wireless telegraphy.

Mr. W. DUDDELL asked if the discharge through the X-ray bulb in the experiment shown at the meeting was unidirectional.

Prof. J. A. FLEMING asked if the coil could be used for medical work. He also asked if the frequency of the discharge could be made high enough for wireless telegraphy, and commented on the small amount of sparking at the commutator.

Dr. R. S. WILLOWS suggested that the nature of the discharge in the secondary could be easily determined by using a vacuum tube rectifier.

Mr. ADDENBROOKE asked how much energy could be obtained from the secondary of the coil exhibited.

Prof. WILSON replying, said the adjustment was performed experimentally. Using an air-coil for primary, enormous frequencies could be obtained in the secondary. The efficiency of the instrument was high compared with that of ordinary coils. The electromotive force induced in the secondary was oscillatory, but in the experiment shown the X-ray bulb acted as a rectifier.

A paper on "*The behaviour of Steel under combined Static Stress and Shock*" was read by Mr. F. ROGERS.

Attention is drawn to the importance of the time rate of increase of stress, ds/dt, in the behaviour of materials under stress. The exact determination of this rate must usually present much difficulty, but the indirect experimental method adopted consisted in submitting specimens of steel to shock whilst under static loading. The machine used for this purpose was exhibited and described at the meeting, and contained some novel features. The important conclusion that steel is substantially less resistant to shock whilst it is under static stress, appears to be definitely established by these experiments. In some cases the effect of a large static stress was to diminish the resistance to shock by as much as 30 per cent.

It is noteworthy that the correction for the work done upon the sample in applying the static load is relatively small. Thus, the energy absorbed in breaking a sample of steel is greater when entirely applied as shock, than when applied partly as shock and partly statically. This difference is considered to be due chiefly to the difference in the rate of increase of stress at the higher stresses in the two cases. The actual values of the highest stresses are not necessarily identical, but probably the higher the rate of increase of stress, the higher is the greatest stress reached before rupture occurs; whilst simultaneously deformation is diminished, and the intimate nature of the breakdown suffers a corresponding variation. An explanation depending directly upon the nature of intermolecular forces is so conjectural in the present state of knowledge that it is not pressed. At the higher static loads employed some portions of the test-pieces were stressed beyond their elastic limits, and this may also help to account for a part of the diminution in resistance to shock—a factor to which the author is, however, inclined to attach comparatively little weight, because a piece of steel which has been over-strained statically is not necessarily thereby made more brittle. The importance of the effect of internal stresses in steel upon its resistance to shock is emphasised in view of the present result.

Mr. R. S. WHIPPLE asked if the same results were obtained with high and low carbon steels, and whether the results were affected by annealing.

Mr. ETCHELLS asked what the author meant by "calculated extreme static stress," and also how the stress was applied. It was difficult to calculate the stress in the author's experiments.

Prof. SMITH said the paper opened up a field for research, and then described some experiments which he had been making recently on the time rate of change of strain.

The AUTHOR, in reply to Mr. Whipple, said he had obtained the same results from steels with carbon varying from 0·16 to to 0·45 per cent. The actual apparatus was exhibited, and the manner in which the stress was applied was shown.

NOTICES OF BOOKS.

The Relations between Chemical Constitution and some Physical Properties. By SAMUEL SMILES, D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1910.

THE physical properties which have been chosen for consideration in this volume are classified as mechanical properties, such as capillarity and viscosity, thermal properties such as specific heat, and optical properties such as refractive and dispersive power, and absorption of light. Some important physical properties are omitted, including crystalline form, optical rotatory power, electric conductivity, and heat of combustion, either because they have been adequately dealt with in other volumes belonging to the same series of Text-books of Physical Chemistry, or because their relation to chemical constitution is not sufficiently understood for definite statements to be made. The point of view is chiefly that of organic chemistry, and the author has endeavoured to meet the needs both of the general student of chemistry and of the more advanced worker who is carrying on a research in the subject. To fulfil this double aim is obviously a matter of considerable difficulty, but on the whole the book represents a successful attempt. The full references to original papers make further reading easy to select, and the subject is treated more or less practically, the application of each method of determining constitution from a study of physical constants being carefully explained. The whole subject is excellently summarised in a final chapter, in which the author touches upon the problem of the nature of valency.

Allen's Commercial Organic Analysis. Volume III. Fourth Edition. Edited by W. A. DAVIS, B.Sc., A.C.G.I., and SAMUEL S. SADTLER, S.B. London: J. and A. Churchill. 1910.

VOLUME III. of the new edition of "Allen's Commercial Organic Analysis," which is now in course of publication, deals with three groups of compounds, the Bitumens (including Aromatic Hydrocarbons and Phenols), the Aromatic Acids, and modern Explosives. The great variety of new

substances belonging to these groups which have come into use during recent years has necessitated the preparation of a practically new book, in which the most rapid and satisfactory methods of analysis are ably described. In the case of explosives United States as well as British tests are given, and every effort has been made to make the book equally useful on both sides of the Atlantic, and to introduce uniformity in weights and measures, nomenclature, &c. The editorial work of Dr. Leffmann has now been undertaken by Mr. S. S. Sadtler, of Philadelphia, and the publication of the concluding volumes of the work is being pushed on as quickly as possible.

Conduction of Electricity through Gases and Radio-activity. By R. K. McClung, M.A., D.Sc. London: J. and A. Churchill. 1910.

The time is certainly at hand when every student of chemistry who wishes to lay claim to a thorough knowledge of his subject must have studied the phenomena of radio-activity both in theory and practically, and a book such as this which provides him with a complete though not exhaustive course on the subject will be heartily welcomed. It discusses the theory of the conduction of electricity through gases and radio-activity, and, in addition, describes in detail a series of experiments to illustrate the text. Apparatus is fully explained with the aid of diagrams, and special care is taken to point out difficulties and probable sources of error, and to prevent the student from being bewildered by apparently contradictory results, which may be due to slight mistakes in experimental arrangement or manipulation. The book is excellently suited for the use of college students, and will be invaluable as a preparation for research work in radio-activity.

Physical Chemistry. By James C. Philip, M.A., Ph.D., D.Sc. London: Edward Arnold. 1910.

Students of biology, physiology, and medicine, for whom this book is specially intended, have hitherto had great difficulty in following the extraordinarily rapid advance of physical chemistry, and its application to the sciences in which they are specially interested, and they will have every reason to be grateful to the author of this book for the excellent exposition he has given of the principles of physical chemistry. All his illustrations and examples are chosen from biology; for example, under diffusion phenomena the passage of carbon dioxide through the stomata is discussed, and colloidal chemistry is specially considered in its relation to biology and vital phenomena generally. The book is written in a most interesting style, and is well up to date; thus Loeb's work on the artificial fertilisation of sea urchins' eggs is discussed, and the references to original papers extend down to 1909.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xliii., No. 11, 1910.

Preparation and Molecular Weight of Hypophosphoric Acid.—Arthur Rosenheim and Jacob Pinsker.—Corne's method of preparing hypophosphoric acid—fusing yellow phosphorus in a solution of copper nitrate—gives satisfactory results, and a good yield can also be obtained by the anodic oxidation of phosphorus, metallic phosphide being used as anode, and the metal of the phosphide as cathode, in a bath made slightly acid with sulphuric or formic acid. Copper phosphide is specially suitable for this purpose. After the removal of the heavy metal from the electrolyte half of it is made neutral with sodium carbonate, and added to the other half. The whole is then evaporated down when $NaHPO_3 + 2H_2O$ crystallises out. The difficultly soluble very characteristic guanidinium subphosphate is a convenient salt for detecting hypophosphoric acid. Cryoscopic determinations show that the molecule of hypophosphoric acid is H_2PO_3, which undergoes association in aqueous solution, giving complexes $(H_2PO_3)x$.

New Thorium Salts. — Georges Karl. — Thorium picrate, $Th(C_6H_2N_3O_7)_4 + 10H_2O$, is obtained by the addition of ammonium picrate to a hot aqueous thorium nitrate solution. It has a low melting.point (52—53°), and explodes when heated in a naked flame. The anhydrous picrate is a glassy yellow substance which does not become liquid at 100°. By the addition of the calculated amount of ammonium hippurate to an aqueous solution of thorium nitrate the white crystalline hippurate, $(C_6H_5.CO.NH.CH_2.COO)_4Th$, is precipitated. The author has prepared the following basic thorium chloracetates:—The monochloracetate, $(ClCH_2.COO)_2Th(OH)_2 + H_2O$; the dichloracetate, $(Cl_2CH.COO)_2Th(OH)_2$; and the trichloracetate, $(Cl_3C.COO)_2Th(OH)_2$.

Zeitschrift für Anorganische Chemie.
Vol. lxviii., No. 1, 1910.

Ammoniacal Mercuric Bromide Compounds. — Ragnar Widman.—The following compounds, $HgBr_2.2H_3N$, H_2NHgBr, $NH(HgBr)_2$, $Hg_9N_4Br_6$, NHg_2Br, can exist as solid phases in equilibrium with solutions which contain H_4NBr, H_3N, and $HgBr_2$ in different proportions. Probably these are the only compounds that can exist thus. The compound $NH(HgBr)_2$, the existence of which has been proved by this research, is interesting, for, adopting Pesci and Rammelsberg's method of formulation, its formula can be written $(NHg_2Br + HBr)$. NHg_2Br is canary yellow, $Hg_9N_4Br_6$ is yellowish brown, and the other compounds are white.

Separation of Antimony and Tin by Distillation.—W. Plato.—Antimony and tin can be quantitatively separated by distillation, and the same method can be applied to the quantitative separation of antimony, tin, and arsenic from one another and from the heavy metals, especially copper and lead. The method depends upon the behaviour of antimony and tin when they are distilled in a current of hydrochloric acid from a sulphuric acid solution to which phosphoric acid has been added. The tin combines with the phosphoric acid to form tin phosphoric acid, provided that the temperature is not allowed to exceed a definite limit (155—165°), and the antimony can be distilled off. Then the temperature is raised, hydrobromic acid is added, and the tin is distilled off.

Autodecomposition of Permanganates and Permanganic Acid.—Anton Skrabal.—The author has already investigated the reducing action of organic substances on potassium permanganate, upon which subject Sarkar and Dutta have recently published a paper (*Zeit. Anorg. Chem.*, 1910, lxvii., 225). The author's scheme showing the reactions is as follows:—

$$Mn^{VII.} \rightarrow Mn^{II.} + O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

$$Mn^{II.} + Mn^{VII.} \rightarrow Mn^{III.} \rightarrow \begin{cases} Mn^{II.} + Mn^{IV.} & . \quad (2). \\ Mn^{II.} + O_2 & . \quad . \quad (3). \end{cases}$$

$$Mn^{IV.} \rightarrow Mn^{II.} + O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

This differs from that of Sarkar and Dutta in the equation marked (3), but it is found that the evolution of oxygen is most rapid during the reduction of the permanganate and not after it is over. Hence all the oxygen cannot be evolved during the reaction expressed by equation (4) as Sarkar and Dutta assume.

Separation of Copper from Cadmium and Zinc by means of "Cupferron."—Josef Hanus and Arn Soukup.—Copper can be separated from acid solution by means of

"cupferron" (ammonium nitrosophenylhydroxylamine) if the reagent is present in excess and the filtration is performed immediately after precipitation. Cadmium and zinc are not precipitated in acid solution, but can be determined in the filtrate as basic carbonates after the destruction of the excess of cupferron by means of nitric acid and the evaporation of the solution.

Sulphurous Acid as an Etching Materialt or Metallographic Purposes.—Siegfried Hilpert and Edward Colver-Glauert.—Commercial aqueous sulphurous acid when diluted with twenty-five times its volume of water makes an excellent etching agent for iron for metallographic purposes, and the authors describe in detail the results they have obtained with various alloys of iron, using this method of etching.

MISCELLANEOUS.

Physical Society's Exhibition.—The date of the annual Exhibition held by the Physical Society of London, which was fixed some time ago for December 13th, has been altered to Tuesday, December 20th. The Exhibition will be open in the afternoon as well as in the evening.

Royal Institution.—The Eighty-fifth Christmas Course of Juvenile Lectures, founded at the Royal Institution in 1826 by Michael Faraday, will be delivered this year by Prof. Silvanus P. Thompson, D.Sc., F.R.S., M.R.I., his subject being "Sound, Musical and Non-musical; A Course of Experimental Acoustics." The lectures will be delivered on the following days, at 3 o'clock: Thursday, December 29, December 31, 1910; January 3, 5, 7, and 10, 1911.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th instant, Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. T. B. Browne, Prof. H. S. Hele-Shaw, F.R.S., Mr. A. C. Hurtzig, Dr. A. Latham, Mr. W. Newall, Mrs. H. Gordon Shee, and Dr. St. Clair Thomson were elected Members. The Special Thanks of the Members were returned to Mrs. Tyndall for her valuable gift of two Nicol's Prisms, constructed for the Lectures on Light given by Dr. Tyndall in America in 1872, and used by him subsequently in his researches and lectures; also two pieces of rocksalt, the remains of a large block given to Dr. Tyndall by the King of Wurtemberg in 1867.

Wilted Weeds.—In *Knowledge* for November, Mr. Harold Long concludes his consideration of the chemical means by which weeds may be destroyed, and it is really surprising what has been accomplished in this direction. It appears that the following weeds, which are of special interest to farmers in this country, may be eradicated or largely subdued in grain fields by the use of chemical sprays:—False flax, charlock, shepherd's purse, corn-cockle, chickweed, dandelion, creeping thistle, bindweed, and plantain. Sulphate of copper and sulphate of iron are the materials chiefly used, but calcium cyanamide has also been found useful for destroying charlock in corn crops. Two photographs are reproduced of a lawn infested by dandelions; one shows thousands of heads of fruit on an area untreated by iron sulphate before blossoming time, and the other a different part of the same plot over which the chemical had been thrown by a traction sprayer two weeks before the plants came into flower and on which there is only a dandelion head, here and there.

Prize for the best Method for the Determination of Quinine in Cinchona Bark.—The Preanger Kinabond at Bandong (Java, Dutch East Indies) offers a prize of five hundred guilders (f. 500) for establishing the best method of determining quinine in cinchona bark. The result of the analysis should indicate to a nicety the real quantity of quinine in the bark, and the accuracy of the process has to be such that, when effecting parallel analyses, differences must not exceed 0·2 per cent (two-tenths per cent). The time required for the analysis as well as its cost will also form points of judgment. In the description of the method of analysis no detail whatever should be omitted. Competitions, either in Dutch, French, English, or German, are to reach the Secretary of the Preanger Kinabond at Bandong at the latest one year after the insertion of the prize-subject in the periodicals. They are not to be delivered in the handwriting of the author, but must be signed by a motto, which should be repeated on the sealed envelope, containing a note bearing name and address of the author, accompanying his essay. The essays will be criticised in the same periodicals in which the competition has been opened, and the Preanger Kinabond is entitled to publish the prize essay, disclosing name and address of the author. Unless specially asked for by the writer the other essays are torn up. Messrs. Prof. Dr. P. van Romburgh, Utrecht; Prof. Dr. N. Schoorl, Utrecht; and Mr. P. van Leersum, Manager of the Government Quinine Establishments, will act as umpires.—For the Preanger Kinabond, (Signed) J. A. VAN RIEMSDIJK, Secretary.

NOTES AND QUERIES.

'*,* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Artificial Camphor.—Can any correspondent supply the names and addresses of English manufacturers of artificial camphor?—A.

Specific Gravity of Chalk.—In what degree is the specific gravity of crude chalk altered by—(1) Being purified; (2) or prepared for chemists? Also, does the (geological) upper and lower formation of chalk differ much in specific gravity—the upper being generally flinty and the lower soft and marly?—T.

Chemical Products and Manufactures.—I desire to ascertain information on the following, and in the hope that you may be able to afford some details I venture to apply to you:—(*a*) Method and cost of manufacture, quantity exported, &c., of precipitated chalk. (*b*) Approximate production, import, export, and sources from which obtained of—(1) Sodium carbonate, (2) calcium carbonate, (3) magnesium carbonate, (4) barium sulphate. If it be in your power to assist me with some details covering these points I shall deeply appreciate the courtesy. The official statistics do not mention these chemicals under their separate names, and reference to the Customs Statistical Branch has resulted in a reply to the effect that they are classed under the heading of "Chemical Products and Manufactures."—A. NUTTING.

MEETINGS FOR THE WEEK.

WEDNESDAY, 16th.—Microscopical, 8. Exhibition of specimens of British Mycetozoa, by A. E. Hilton.

THURSDAY, 17th.—Royal Society. "Effect of Gravity upon the Movements and Aggregation of *Euglena viridis*, Ehrb, and other Micro-organisms," by H. Wager. "Influence of Bacterial Endotoxins on Phagocytosis, including a New Method for the Differentiation of Bacteria," by L. S. Dudgeon, P. N. Panton, and H. A. F. Wilson. "State of Aggregation of Matter Part I., Action of Salts in Heterogeneous Systems, and on the Nature of the Globulins; Part II., Action of Formaldehyde on Witte's Peptone; Part III., Solubility of Phenol and certain Crystalline Substances in Salt Solutions," by S. B. Schryver. "Proteolytic Enzyme of Drosera," by Miss J. White. "Method for Isolating and Growing the Leprosy Bacillus of Man," by F. W. Twort. "Oxidation of Phenol by certain Bacteria in Pure Culture," by G. J. Fowler, E. Ardern, and W. T. Lockett.

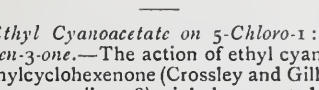
— — Chemical, 8.30. "Preparation of Secondary Amines from Carboxylic Acids—Part I., Preparation of Heptadecylaniline, Pentadecylaniline, and Tridecylaniline," by H. R. Le Sueur. "Wet Oxidation of Metals—I., The Rusting of Iron," by B. Lambert and J. C. Thomson. "Action of Sodium Amalgam on Methylene Ethers," by A. H. Salway. "Homogeneous Decomposition of Ozone in the presence of Oxygen and other Gases," by D. L. Chapman and H. E. Jones. "Addition of Bromine to Unsaturated Compounds," by J. J. Sudborough and J. Thomas. "Colour and Constitution of Diazonium Salts—Part III., The Diazo-derivatives of 2:7-Naphthylenediamine," by G. T. Morgan and Miss F. M. G. Micklethwait.

THE CHEMICAL NEWS.

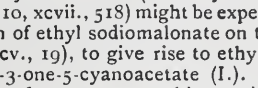
Vol. CII., No. 2660.

THE STUDY OF HYDRO-AROMATIC SUBSTANCES.*

Action of Ethyl Cyanoacetate on 5-Chloro-1 : 1-dimethyl-Δ^4-Cyclohexen-3-one.—The action of ethyl cyanoacetate on chlorodimethylcyclohexenone (Crossley and Gilling, *Journ. Chem. Soc.*, 1910, xcvii., 518) might be expected, by analogy with the action of ethyl sodiomalonate on the same ketone (*Ibid.*, 1909, xcv., 19), to give rise to ethyl 1 : 1-dimethyl-Δ^4-cyclohexen-3-one-5-cyanoacetate (I.). But although the reaction product possesses this empirical formula, it has properties which are incompatible with those of a substance of this constitution, for it behaves as a monobasic acid, forming compounds by elimination of water with aniline and monomethylaniline, and giving esters when heated with alcohol containing 5 per cent sulphuric acid. In the latter case two isomeric methyl or ethyl derivatives are produced. When hydrolysed with acids, both the original condensation product and either of its ethyl or methyl derivatives are transformed into trimethylcyclohexenone (II.).

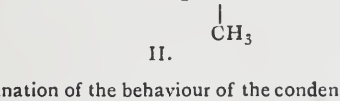


I.

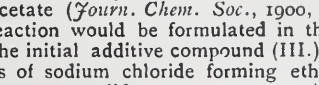


II.

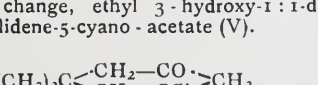
An explanation of the behaviour of the condensation product is afforded by adopting Thorpe's formula for ethyl sodiocyanoacetate (*Journ. Chem. Soc.*, 1900, lxvii., 925), when the reaction would be formulated in the following manner. The initial additive compound (III.) would lose the elements of sodium chloride forming ethyl 1 : 1-dimethylcyclohexen-3-onylidene-5-cyanoacetate (IV.) and by tautomeric change, ethyl 3-hydroxy-1 : 1-dimethyl-Δ^3-cyclohexenylidene-5-cyano-acetate (V).



III.

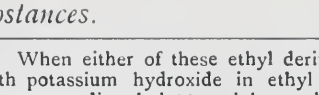


IV.

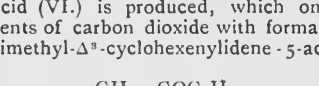


V.

The last formula accounts for all the observed properties of the substance including its ability to form two ethyl derivatives which can be represented as *cis* and *trans* modifications. When either of these ethyl derivatives is hydrolysed with potassium hydroxide in ethyl alcoholic solution 3-ethoxy-1 : 1-dimethyl-Δ^3 cyclohexenylidene-5-cyanoacetic acid (VI.) is produced, which on heating loses the elements of carbon dioxide with formation of 3-ethoxy-1 : 1-dimethyl-Δ^3-cyclohexenylidene-5-acetonitrile (VII.).

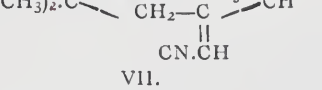


VI.



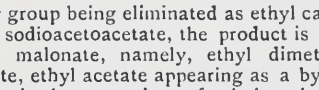
VII.

Although somewhat stable towards alkali this nitrile is readily hydrolysed by acids with formation of 1 : 1 : 5-trimethyl-Δ^4-cyclohexen-3-one (II.). When chlorodimethylcyclohexenone is condensed (*a*) with the sodium derivative of ethyl methylcyanoacetate the product is hydroxydimethylcyclohexenylidenepropionitrile—



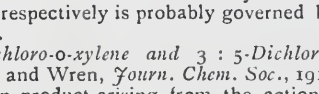
the carbethoxy group being eliminated as ethyl carbonate ; (*b*) with ethyl sodioacetoacetate, the product is the same as with ethyl malonate, namely, ethyl dimethylcyclohexenoneacetate, ethyl acetate appearing as a by-product. The elimination in these reactions of ethyl carbonate and ethyl acetate respectively is probably governed by spatial considerations.

2. *3 : 5-Dichloro-o-xylene and 3 : 5-Dichlorophthalic Acid* (Crossley and Wren, *Journ. Chem. Soc.*, 1910, xcvii., 98).—The main product arising from the action of phosphorus pentachloride on dimethyldihydroresorcin (I.) is 3 : 5-dichloro-1 : 1-dimethylcyclohexadiene (II.), but a by-product is also formed which was thought to be 3 : 5-dichloro-*o*-xylene (III.).



I.

II.



III

This structure was assigned to the latter substance because there did not appear to be any reason to presume that, in the conversion of the hydroaromatic into the aromatic dichloro-derivative, the chlorine atoms would alter their positions. During the reaction, however, a methyl group must have wandered, and this was shown to have migrated to the ortho-position, because on oxidation an acid (3 : 5-dichlorophthalic acid) was obtained which readily gave an anhydride, and also the fluorescein reaction.

In a recent number of the *Berichte* (1909, xlii., 3529), Villiger described the preparation of three of the four possible dichloro-*o*-phthalic acids (Cl : Cl, 3 : 6, 3 : 4, 4 : 5) by the direct chlorination of phthalic anhydride. Villiger points out (*Ibid.*, p. 3532) that a fourth isomeride was described by Crossley and Le Sueur in 1902 (*Trans.*, lxxxi., 1533), and regards the acid as 3 : 5-dichloro-*o*-phthalic acid, although "its constitution has never been controlled."

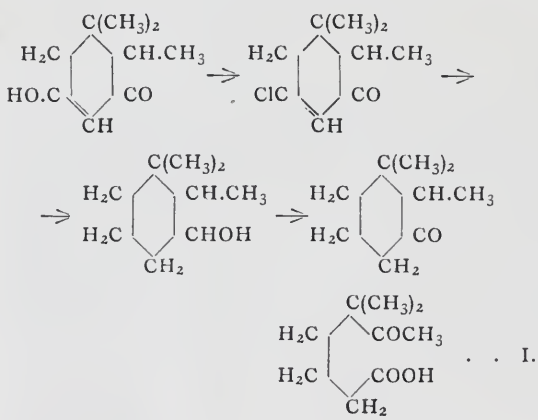
3 : 5-dichloro-*o*-xylene has now been prepared from 3 : 5-dinitro-*o*-xylene by means of the diazo reaction, and oxidised to 3 : 5-dichlorophthalic acid. A detailed comparison of the properties of these synthetic products with those obtained as above mentioned from dimethyldihydroresorcin

* Report of the Committee, consisting of Dr. E. Divers (Chairman), Prof. A. W. Crossley (Secretary), Prof. W. H. Perkin, Dr. M. O. Forster, and Dr. H. R. Le Sueur. Read before the British Association (Section B), Sheffield Meeting, 1910.

shows them to be identical, as seen from the following tabulated statement :—

	From dimethyldihydroresorcin.	From 3 : 5-dinitro-*o*-xylene.
Dichloroxylene.. ..	Yellow refractive liquid ; slight aromatic odour. B.p. 226°, m.p. 3—4°.	Yellow refractive liquid ; slight aromatic odour. B.p. 226°, m.p. 5—7°.
Dichlorodinitroxylene	M.p. 175—176°.	M.p. 176°.
Dichlorophthalic acid	M.p. 164° (previous softening) with evolution of gas.	M.p. 164° (previous softening) with evolution of gas.
Dichlorophthalic anhydride	M.p. 89°.	M.p. 89°.
Dichlorophthalanil ..	M.p. 150—150·5°.	M.p. 150°.

Hydro-aromatic Ketones (Unpublished work).—In continuation of the work previously described (Crossley and Renouf, *Journ. Chem. Soc.*, 1907, xci., 63), 1 : 1 : 2-trimethylcyclohexan-3-one has been prepared from trimethyldihydroresorcin as a starting point, the various steps involved being indicated by the following formulæ :—



. . I.

1-1 : 2-trimethylcyclohexan-3-one is a colourless liquid, boiling at 190°/750 mm., and when oxidised with potassium permanganate yields δ-acetyl-δ-methylhexoic acid (I), which fact definitely establishes its constitution. The investigation of this ketone is being continued, partly on account of the similarity in the groupings which it contains with those of the camphor molecule.

Royal Society of Arts.—The Programme for the One Hundred and Fifty-seventh Session of the Royal Society of Arts is being issued to the Members. There will be five Ordinary Meetings before Christmas, at the first of which the usual Address was given by the Chairman of the Council, Sir John Cameron Lamb. The papers announced for the other four meetings are by Sir Henry H. Cunynghame, K.C.B., "Detecting Fire-damp"; Mr. C. P. Ogilvie, "Argentina"; Dr. Vaughan Cornish, "The Panama Canal"; and Mr. Reginald Smith, "Roman London." There will also be a meeting of the Colonial Section, at which Mr. A. Montgomery will read a paper on "Mining in Western Australia," and one of the Indian Section to be occupied by a paper by Mr. R. F. Chisholm, on "The Taj Mahal." On the four Mondays before Christmas Mr. C. R. Darling is to give a course of Cantor Lectures on "Industrial Pyrometry." There is also a very full list of papers and lectures for the part of the Session after Christmas.

BANQUET TO PAST-PRESIDENTS OF THE CHEMICAL SOCIETY.

NOVEMBER 11, 1910.

THE Banquet to the Past-Presidents who have been Fellows of the Chemical Society for more than half a century :—

	Elected.	Served as President.
Prof. WILLIAM ODLING, F.R.S. . ..	1848	1873—1875
The Rt. Hon. Sir HENRY E. ROSCOE, F.R.S...	1855	1880—1882
Sir WILLIAM CROOKES, O.M., F.R.S.	1857	1887—1889
Dr. HUGO MÜLLER, F.R.S.	1859	1885—1887
Dr. A. G. VERNON HARCOURT, F.R.S.	1859	1895—1897

was held at the Savoy Hotel on Friday November 11th, 1910, Prof. HAROLD B. DIXON, F.R.S., President, in the Chair.

To the regret of all present the Right Hon. Sir Henry Roscoe was not well enough to be present; his reply was read by the President.

More than 250 Fellows and Guests were present, among them being—His Grace the Duke of Northumberland, K.G., P.C., F.R.S., President of the Royal Institution; The Rt. Hon. H. L. Samuel, Postmaster-General; Prof. W. Odling, F.R.S., Past-President; The Rt. Hon. Lord Strathcona and Mount Royal, G.C.M.G., G.C.V.O., F.R.S., Chancellor of the University of Aberdeen; Prof. Albin Haller, Président de la Société Chimique de France; Sir William Crookes, O.M., F.R.S., Past-President; Prof. Dr. Otto Wallach, Präsident der Deutschen Chemischen Gesellschaft; Herr Generaldirektor S. Eyde; Dr. Hugo Müller, F.R.S., Past-President; Dr. A. G. Vernon Harcourt, F.R.S., Past-President; The Rt. Hon. Lord Justice Buckley; Sir Archibald Geikie, K.C.B., F.R.S., President of the Royal Society; Sir Edward Thorpe, C.B., F.R.S., Past-President; Prof. J. E. Reynolds F.R.S., Past-President; Sir Arthur Rücker, F.R.S.; Prof. J. H. Poynting, F.R.S.; Prof. H. E. Armstrong, F.R.S., Past-President; Sir William A. Tilden, F.R.S., Past-President; Sir James Dewar, F.R.S., Past-President; Sir James Crichton-Browne, F.R.S., Treasurer of the Royal Institution; Sir Alfred Keogh, K.C.B., Rector of the Imperial College of Science and Technology; Sir William Ramsay, K.C.B., F.R.S., Past-President; Sir F. Carruthers Gould; Sir George Frampton, R.A.; Prof. R. Meldola, F.R.S., Past-President; Prof. F. S. Kipping, F.R.S., Vice-President; Prof. W. J. Pope, F.R.S.; Dr. R. Messel; Dr. A. E. H. Tutton, F.R.S.; Dr. J. C. Cain, Editor; A. J. Greenaway, Sub-Editor; C. E. Groves, F.R.S.; Dr. G. T. Morgan, Hon. Secretary; Dr. J. F. Thorpe, F.R.S.; Prof. W. R. E. Hodgkinson; Prof. P. F. Frankland, F.R.S.; Prof. W. H. Perkin, F.R.S.; Prof. E. Rutherford, F.R.S.; Sir Alexander Pedler, C.I.E., F.R.S.; Prof. J. M. Thomson, F.R.S.; Prof. J. J. Dobbie, F.R.S., Vice-President; Dr. J. J. H. Teall, F.R.S., Director of the Geological Survey; Sir Arthur H. Church, K.C.V.O., F.R.S.; Prof. G. Carey Foster, F.R.S.; Prof. E. Divers, F.R.S.; Rev. Canon T. G. Bonney, F.R.S., Pres. Brit. Assoc.; Henry T. Butlin, Pres. Roy. Coll. of Surgeons; Dr. G. T. Beilby, F.R.S., President Inst. of Chemistry; Prof. W. W. Watts, F.R.S., President Geological Society; Prof. W. R. Dunstan, F.R.S.; Sir E. Ray Lankester, K.C.B., F.R.S.; Dr. R. T. Glazebrook, Pres. National Physical Laboratory; Sir Andrew Noble, Bart., K.C.B., F.R.S.; Dr. A. Scott, F.R.S., Hon. Treasurer; Sir Joseph Larmor, F.R.S., Secretary of the Royal Society; Sir J. Norman Lockyer, K.C.B., F.R.S., Chairman of the British Science Guild; Principal Silvanus P. Thompson; James Swinburne, F.R.S., President of the Faraday Society; Walter F. Reid, President of the Society of Chemical Industry; Sir John Wolfe-Barry, K.C.B., LL.D., F.R.S., Chairman of Executive Committee of the City and Guilds of London Institute; Dr. H. A. Miers, F.R.S., Principal of London University; Dr. J. Rose Bradford, F.R.S., Secretary of

the Royal Society; E. W. Voelcker, Pres. The Society of Public Analysts; Dr. M. O. Forster, F.R.S., Vice-Pres.; Prof. W. P. Wynne, F.R.S.; Prof. A. W. Crossley, F.R.S., Hon. Secretary; Dr. E. C. Seaton; Sir Boverton Redwood; Sir John Forsey, Director of Naval Stores; A. G. Gordon Salamon; Sir Richard Garton; R. B. Pilcher, Registrar of the Institute of Chemistry; H. Crookes; Dr. A Liversidge, F.R.S.; Vice-President; Prof. D. O. Masson, F.R.S.; F. W. Clifford, Librarian.

After the usual Loyal Toasts had been honoured the President, in proposing the Toast of the "Past-Presidents who have been Fellows for Half a Century," said—

Although I believe in the general truth of Thackeray's dictum that public speaking after dinner ought to be done—like the carving—by a skilful person at a side-table, still there are occasions when the heart itself must speak, however unskilful the utterance, for is it not true that—

> "All hearts in love use their own tongues,
> And trust no agent?"

I know I utter something of that which is in the hearts of all our Fellows to-night when I offer to you, our honoured Past-Presidents, in the name of the Chemical Society, our sincere and loving congratulations on your Jubilee as Fellows; and where I fail, as fail I must, to express the thoughts that are stirring in each of us—*conamur tenues grandia!*—I trust that failure will be put down to the difficulties of the task and to the imperfections of the instrument, and not to any lack of loyalty to my teachers, and not to any want of appreciation of their achievements or of gratitude for the friendships they have given me.

On the one occasion that forms a precedent for this celebration (curiously enough it was on Friday, November 11th, 1898), the distinguished President of that day was able, with the perfervid imagination of the Scot, to classify the Past-Presidents into two divisions—the imperial and the merely regal—and so discussed them more or less *en bloc* and impersonally. Chemists, like other men, have their peculiarities. I have heard myself and my students branded as "anhydrous chemists"; I have heard another school maintain that water is "the only begetter" of chemical action, and I am told there are even chemists who look on wine when it is red and can see in that colour nothing but the evidence of *a quinonoid structure*. But I cannot find in our Past-Presidents any common peculiarities by which I might label them, any natural groups into which I can divide them. At our last matriculation examination I set some question on the halogens, and received as an answer from a young lady, "Chlorine, bromine, and iodine are a very active set of chemicals; so active, indeed, that they are classed under the name of the *Hooligans*." Perhaps if our policy had been different towards those peris who have been knocking at the gate of our chemical paradise, a more imaginative President in my place would have had no difficulty in classifying or in attaching an appropriate label to the "very active set of chemicals" whose health she would have been proposing.

As it is, I must be personal and therefore discriminating in my praise, and you will readily understand that it is no easy matter to make discriminating and impartial remarks about, and in the presence of, one's seniors—especially when one was my university professor and examiner and another was my college tutor. I should be happy if I could reach the impartiality of the dying Irishman, who cried:—"Bury me between my two wives,—but *wisht*, bhoys—push me *just a bit nearer to Biddy!*"

The Society is fortunate to contain on its roll of members twenty-four Fellows of over fifty years standing. To all of these we shall waft our greetings when we drink this toast. Of these Jubilee Fellows we have among us to-night—besides our Past-Presidents—Sir Arthur H. Church (elected (1856), George Carey Foster (elected 1856), P. J. Worsley (elected 1858), John Spiller (elected 1859), and Edward Divers (elected 1860). One name we had originally hoped to include among the Jubilee Past-Presidents, that of the late W. J. Russell; but it was not to be. And another, G. D. Liveing (elected 1853) would have been among the living Presidents had his health been stronger.

I cannot read to you all (or even a selection from) the numerous friendly greetings sent by our colleagues from Europe and America. Luckily we have with us, in the President of the French Chemical Society, Prof. Haller, and in the President of the German Chemical Society, Prof. Wallach, representatives who can tell us with no uncertain voice what European science owes to the labours of our Jubilee Presidents.

But one short passage from a letter headed "Washington," I will read to you:—

"I am sure that I speak the feelings of all American chemists when I say that your guests more than deserve all the honour that can be shown them. Each one has made his permanent mark upon the history of chemical science, and will be remembered so long as chemistry is studied. Each one has been a source of inspiration to American chemists, and is as well known here as in his own home—perhaps better known if perspective counts for anything. When details vanish the great realities can be seen.

With regrets for my absence, and congratulations to the Society and its guests.—Yours sincerely,

Frank Wigglesworth Clarke."

And now for personalities:—

(1) Right Hon. Sir Henry Roscoe.

Fifty-five years ago Henry Enfield Roscoe was elected a Fellow of this Society, and read his first paper "On the Absorption of Chlorine by Water." The "sport" of a literary family, he will, I hope, tell us how the chemist in him was rough-hewn by Alexander Williamson, and how Bunsen shaped the ends—of his fingers. The early years of his manhood he spent with Bunsen at Heidelberg, designing and elaborating that beautiful apparatus for measuring the chemical intensity of light which has been the model for all subsequent investigators. At twenty-five, already known as a brilliant experimentalist, he was elected to the Chair of Chemistry at Manchester.

He came to Owens College in the darkest hour of her fortunes. Gifted with energy and courage, and above all with the power of seeing and drawing out what is good in others. Roscoe not only built up a great school, but he convinced his countrymen that a scientific education must be the corner-stone of our national industry. To be a successful professor in a struggling university, the professor must be—as Mrs. Ram said of Cæsar's wife—"all things to all men." I believe one of the secrets of Roscoe's success lay in his many-sidedness. The man who, in the intervals of teaching, tracked down the true vanadium, and in doing so gave order and meaning to the nitrogen group of elements, that man could turn aside from his researches to design and equip the largest laboratories of the time, could conceive and initiate a scheme which in its natural growth is within measurable distance of giving a university to every great city in the land.

Just twenty-four years ago it was my happy fortune to follow Roscoe at Owens, to breathe the atmosphere he had created, to know something of the devotion with which he was looked up to, to feel something of the stimulus which his presence radiated; and this I think I can truly say, that to his disciples the man was even more than his achievements. However much his students admire him as a researcher, however much they revere him as a teacher, it is his personality they most deeply cherish. The friend who stood by them through evil report and good report, the heart that warmed to them, and the head that studied and understood them, *these* make up the memory of Roscoe that will be his proudest monument, and their lifelong possession.

(2) Sir William Crookes.

Of Sir William Crookes it might be said that somewhere in that fourth state of matter he was the first to explore, he found the *elixir vitæ*, the secret of perpetual youth. It is close on sixty years ago since Hofmann's youthful assistant described to the Chemical Society a new class of bodies—the selenocyanides. Just on fifty years ago the same youth gave us the new element thallium. Again, after some dozen years filled with a variety of experiments, he set our brains whirling with the radiometer, and started with unabated enthusiasm to explore the "chemical vacuum" and to measure the heat of "molecular shock." This led to the spectroscopy of radiant matter and of phosphorescent bodies—work of such refinement that when, twenty years later, argon and afterwards helium were discovered, it was, of course, only natural that these refractory gases should be sent to Crookes's youthful eye to have their lines read and duly mapped. Five years ago the brain that had penetrated the witchery of the opal's colouring turned its searchlight on the diamond, and the mystery of its formation was made plain to all men. For fifty years the rare earths have been his happy hunting grounds; only yesterday that elusive metal, scandium, was rounded up by Crookes, separated from the impurities of its wild companions, and made to mate with numerous respectable organic wives.

On Crookes as an experimental lecturer the mantle of Faraday has fallen. No one, since the master, has come so near the marvellous in experiment; no one has awakened the imagination with more inspiring touch.

I well remember hearing him lecture on the radiometer—I think in 1874; I ought to remember it, for it enabled me next day to pass my first *vivâ-voce* examination in science—very much to the surprise of my friends. The examiner had not seen the radiometer, and I managed to get him to take such an interest in its proceedings that he forgot to plough me. Again, at Sheffield in 1879, I listened to the wonderful lecture on Radiant Matter. I thought the brilliancy of experiment could go no further; but since then I have been with Sir William in South Africa and seen the men of Kimberley—men who knew something about the subject—so carried away by his lecture on diamonds that they demanded that the lecture should be repeated, and, needless to say, this young man repeated it.

I know not what new experimental triumphs Sir William Crookes is contemplating; but this I know, he wears not only the order "For Merit," but a talisman with the motto, "Youth will be served."

(3) Hugo Müller.

Among the many services which Hofmann rendered to English chemistry and to England, a high place must be claimed for his introduction of Hugo Müller to our former President, Warren de la Rue. Pupil of Erdmann at Leipzig, of Wöhler at Gottingen, and of Liebig at Munich, Hugo Müller came to London in 1854 to investigate the chemistry of Burmese naphtha in the laboratory of de la Rue and Co. The young chemist soon found work to his hand in that great factory which required the highest chemical skill and knowledge and the most laborious experiments to carry through; his success was marked by the adoption of many of the processes he discovered or improved. The electrotyping process and lithographic printing were by Müller's labours brought into practical use; for years everyone who fingered a banknote or stuck a postage stamp on a letter came unconsciously into personal contact with Hugo Müller's work. Engrossed as he was in these technical investigations, he yet found time to prosecute what is called pure chemistry—as ours and many other *Journals* bear witness. He was no specialist. He was equally expert in mineral analysis, crystallography, organic synthesis, and the nature of the electric discharge. And his interest in chemistry is as keen to-day as it ever was. I believe he cannot help it—his curiosity is insatiable.

It used to be said that no new discovery in chemistry was accepted on the word of the discoverer; that the experiment was sure to be repeated in some other laboratory, and either confirmed or disproved. I did not believe this until I knew Hugo Müller—now I do.

Men have been raising in London a temple to Science and Technology. If they should seek to enshrine in it a tutelary deity, they need not erect a double-headed Janus to look this way and that, but they might well model a statue from a living man who, looking straight before him, sees science and technology as one and indivisible: that man is our Past-President, Hugo Müller.

(4) A. G. Vernon Harcourt.

To Augustus George Vernon Harcourt my lifelong gratitude is due; for the fact that I am addressing you to-night from this honourable chair is entirely his doing. He found me an outcast from the classical fold, with no shred of scientific covering, and—rather ashamed. He took me to his laboratory and gave me a new interest in life and a career.

There was no care that Harcourt would not lavish on his pupils, no minutiæ of manipulation he would not repeat again and again to us. He noted all slovenliness with a watchful eye, and woe betide the wretch who spilt a drop of mercury! To this day I cannot pass a student's bench, where a speck of mercury lingers, without feeling in my pocket for a letter or a postcard, doubling one end of it like the bow of a boat, and scooping up the truant drop into my paper shovel. I commend the method—it is Harcourt's own; or did he learn it from Brodie or Faraday? Perhaps he will tell us to-night.

No one could be long in the old laboratory at Christ Church under Harcourt without being fascinated by those wonderful experiments of his on the velocity of the reaction between hydrogen peroxide and hydrogen iodide, which came as a revelation to the world of science. I shall never forget the first day I was privileged to assist in these experiments, and was set to watch the colourless liquid in its tall cylinder standing by the seconds-beating clock. If all went well I was told the blue colour would appear after an interval, I think, of two hours, fifteen minutes, and eleven seconds—and I must time its appearance to the tick of a second. As the afternoon wore on and the unexpected did not happen, I confess there were moments when I did not feel as

> "One in whom persuasion and belief
> Had ripened into faith."

But when the second came, and in the twinkling of an eye the blue colour spread through the liquid, I knew I had found the true scientific faith, and that my life was settled for me.

I have heard physicists declare that if they were transported to Mars they would be able to reconstruct there the unit of length from the wave-length of sodium light. Could not we also undertake, if this Society were dumped down on a planet, whose period of rotation and gravity differed from ours, to reconstruct the second, the minute, and the hour by the aid of hydrogen peroxide, potassium iodide, and of "Harcourt and Esson"?

I know many of Harcourt's old students, and I know they feel with me that, whatever advance towards truth and accuracy they may have achieved, they owe it to the teaching and example of him whose one aim has been to seek truth and ensue it.

(5) William Odling.

At his own desire I speak last of the *doyen* of our science, to whom all younger chemists owe a debt of gratitude, though possibly some of us may be unconscious of the magnitude of that debt. We have only to turn up the text-books of fifty years ago and compare them with a certain "Manual of Chemistry—descriptive and theoretical," and with other books inspired by the New Chemistry, to see the marvellous change in the order, the

meaning, and the correlation of chemical facts wrought by the "New Chemist's" *quorum pars magna fuit*—William Odling. His work profoundly influenced the views of his contemporaries. He himself has told us that in the earlier days of the Society, when he was a Secretary, papers were few but discussions were numerous; there is ample evidence to prove if proof were wanting—that in those discussions no one put the new arguments more directly, more clearly, or more cogently than Odling. What impressed me most when I listened to him, a few years later, was his extraordinary clearness of vision. It was this power of seeing things as they really are that made him seem a prophet. Let me give three instances that fastened themselves on my memory. He saw at once the meaning of Andrews' experiments on ozone, and predicted the formula O_3, the formula proved by the later researches of Soret and of Brodie; he saw in hydrogen —not a volatile metal—but "the vanishing point of the hydrocarbons"; he saw in benzene—not a ring of carbon atoms in a plane—but two groups, each of three carbon atoms touching one another, one group resting on the other in space, nearly as Pope and Barlow teach to-day.

One other personal instance of prophetic vision I may mention in confidence; Odling examined me for honours, and (*how* he did it I don't know, for I knew next to nothing at the time) he gave me a first-class. Did he foresee this occasion? Perhaps he saw I had faith—and faith has been defined as "the substance of things hoped for, the evidence of things not seen."

Gentlemen, I know you all rejoice with me that we still have with us Odling, our interpreter and prophet, and we will take care that he shall not be without honour even in his own country.

The following speeches were delivered in response to the Toast:—

Sir Henry E. Roscoe.

Old age has its compensations amidst its many drawbacks. To the man of science one of the chief of these compensations is the kindly appreciation which is paid by the younger workers to those whose most active life-work is over. Such an appreciation the Chemical Society gives us to-night, and this it is which cheers one in our latter days, for, after all, it is the approbation and regard of one's fellow-workers in science which is the great reward.

Then comes memory. The recollection of the great men whom it has been one's good fortune to have known. The friendships which during the varied course of life one has made. The examples which such men have set before one; and even if the comparison of the great things which they have accomplished in science may far outshine one's own efforts, yet to have worked for the same end and to have won only a small prize is something to be grateful for.

To-night our thoughts naturally turn to the distinguished men who have been our Presidents—thirty-one in number. I have known them all with the exception of two (Aikin and Phillips). This is not the occasion nor the place to enlarge upon, or even to mention, the scientific work accomplished by our past Presidents. Indeed, any such account would be unfitting, seeing that you all are as well acquainted with that work as I am.

I may, however, be permitted to recall some few reminiscences of those with whom I have come into more intimate personal contact, and such recollections may be of interest, as to most of you many of our past Presidents are merely names with certain scientific labels attached to them.

Our first President—Thomas Graham (1841-43, 1845-47) —was my master. From his lips I first heard a connected account of our science. His lectures were clear and logical; his experimental illustrations carefully prepared and always successful. He was no orator, nor was he a striking personality, but his students recognised at once in him a master mind; his influence over them was great, and I, for one, shall always feel gratitude to him as my first great teacher.

Next to Graham, and perhaps before him in the influence exerted on myself, comes Williamson (1863-65, 1869-71), a man of a totally different race and character. Graham was a cool and dour Scot, and he was not a laboratory teacher. Williamson brought to London the enthusiasm of Paris and of Giessen, and was essentially a laboratory man. Every day he came down to his laboratory brimful of new ideas, and fired the young blood of his students (with, perhaps, the exception of the Excisemen) with the notion that to be a chemist was the grandest thing in life. These Excisemen, you see, cared more to know how to estimate the excess of water in spirit than to know whether its molecule is to be represented by the symbol HO or H_2O, and were more interested in an easy method for ascertaining the amount of proof spirit than in the amount of proof needed to show that alcohol contained one molecule of the radicle whilst ether contained two.

Those of us who did not hail from Somerset House were, on the other hand, as keen as mustard. We revelled in atomic motion; we thought no end of the four typical forms HCl, H_2O, H_3N, H_4C, and we were enamoured of the compound ethers, and even now, after fifty years, I could select by smell a sample of the seven carbon ethers from amongst a hundred other volatile compounds.

And now you must excuse me if I refer to a personal matter. Hitherto I have abstained from allusion to such matters, because I am speaking rather as an ex-President and as a representative—at least, for the moment—of my four brethren whom you honour together with myself. I have often thought that it might have been more natural if, as a pupil and assistant of Williamson, I had gone to Paris instead of to Heidelberg. I might then have had a chance of continuing the line of research which Williamson inaugurated, and which Laurent Gerhardt and Würtz carried further, such, for example, as the discovery of the anhydrides—a discovery which, indeed, Williamson might have made had he not overlooked the existence of the compound which he afterwards termed chloride of othyl, now known as acetyl chloride. The name and fame of Bunsen were, however, too powerful an attraction to be resisted, and in Heidelberg I found myself in an entirely different atmosphere. Bunsen was not, like Williamson, a "theoretiker"; "one chemical fact is worth a host of theories," he used to say. So I became a follower of the great Heidelberg teacher, but only up to a certain point, for Williamson's influence made me an active disciple of what we then termed the new chemistry, in which Bunsen was not a leader.

Enthusiasm such as Williamson possessed is exhibited in many forms, and in every walk of life makes for success. No great teacher, no great worker in science, creates a school or does epoch-making work without this celestial fire. Williamson possessed it. He did not trouble himself much in grounding us in exact experimentation; I learned that afterwards from Bunsen. But he did more. He set us the example of what it is to be a "Forscher"—of a man in hot pursuit of the unknown. If he did not always gain his goal, his successes were great, and his consequent influence has been signal and lasting, not only on those who were fortunate enough to benefit from his example and to enjoy his friendship, but on the chemical world at large.

Perhaps of wider and more public renown was Hofmann (1861-63). He raised the tone of English opinion as to the position which chemistry must hold in the body politic. He gained a respect for chemical research amongst the higher classes of society in this country which had hitherto been but slightly acknowledged. And he was a born expositor in a language foreign to his own. I shall never forget a lecture delivered by him in the old lecture theatre in Faraday's laboratory down in the cellars of the Royal Institution on the early wonders of the coal-tar colour industry. It was, indeed, an incalculable loss to British chemistry when he was called back to the fatherland.

Then there comes before my mind's eye the face and figure of my dear friend Brodie (1859-61), a devoted

worker in our science—a man whose heart was set upon promoting the cause of science at Oxford, and open to all progressive ideas, both scientific and educational.

Frankland (1871-73) was my predecessor at Owens. He is another of the *Dei majores* of our Presidents, for he, like Williamson—and, may I add, like Odling?—laid a foundation stone of Modern Chemistry.

Then follow the names—the respected, well-known names—of De la Rue (1867-68, 1879-80); Abel (1875-77); Gladstone (1877-79); Gilbert (1882-83); and last, but not least, Perkin (1883 85) and Russell (1889-91). These good friends are happy memories to all of us. They "their tasks have done, home have gone, and ta'en their wages." All were remarkable in their several directions—all distinguished by their love of the science and by their devotion to the welfare of the Society.

Of our living ex-Presidents, and of our distinguished Chairman, I will not speak, except to say that they hold (and in this I am vain enough to place myself) in the esteem and regard of the Fellows a position equal to that which we all assign to the memory of those who have gone before. If Britain has held and continues to hold a high position in the science of chemistry—and who shall say, in looking back at our history, that her claim to the first place is unfounded?—I think it equally true that the names of our Presidents are those of good men and true who have worthily sustained the high position of representatives of British chemistry, and of whom the Society may well be proud.

As for the Society itself I have watched, from near and far—farther now than nearer, I am sorry to think—its rise and development for more than half a century, and you will agree with me when I say that at no former period has it shown more life and done more to advance our science than it is doing at the present moment.

For myself, I thank you all from the bottom of my heart for the honour you have done me. This will remain a red-letter day with me to the end of my life.

Sir William Crookes.

A retrospect—a long retrospect—ought to make me melancholy. But to-night, as I stand before you, I feel elated, not depressed. "What more felicitie can fall to creature" than to realise the wild dreams of Youth. It has been accorded to me, for more than two generations, to devote myself amid happy surroundings to the magic work of original research in Chemistry and the allied Sciences. Work, I have always found, is its own exceeding great reward, and now to-night there is the added reward of your approval. But to reach one's Chemical Jubilee is not altogether a matter for joy-bells. When Bret Harte was felicitated on his fiftieth anniversary he replied he could understand a man shooting at his best friend from behind a hedge—but he could not understand how anyone could congratulate him on being fifty!

We can all recall Tyndall's invocation to the "Scientific Use of the Imagination." Tyndall was right. I may truly say that what success I have achieved in Science I owe to Imagination. It has helped me to track anomalies and residual phenomena, for these most frequently act as finger-posts along the high road of research, directing those who can interpret their symbols to bye-ways where lurk the mysteries. An inward prescience, a grasp of events before they occur, is indispensable to pure abstract research. But it must be used with judgment, for a preconceived idea is a dangerous travelling companion to a Researcher. An eminent French chemist once warned his pupils that in scientific research, unless they were careful indeed, they would generally find what they looked for!

But not only are anomalies finger-posts, they sometimes perform more active functions. Frequently they are responsible for what Huxley called "The Great Tragedy of Science,"—the slaying of a beautiful hypothesis by an ugly fact. I fear the radiometer has been guilty of more than one tragedy of this kind. But the whirligig of time brings its revenges, and my friend Sir James Dewar, by his researches on high vacua and low temperature, now threatens to kill the radiometer!

I will take a brief glance backwards. My old master and dear friend Hofmann first started me on the road of Research. About the year 1850 he proposed I should commence an investigation on the "Selenocyanides," using for this purpose some selenium I had extracted from seleniferous residues he had brought from Tilkerode. The result of this research was published in 1851 in the *Quarterly Journal of the Chemical Society*.

When first I entered the Royal College of Chemistry, Liebig was in the height of his fame; his "Chemistry in its Application to Agriculture" would be a useful text-book to-day. In this book was first declared the importance—nay the absolute necessity—of mineral matter and nitrogen to the well-being of the vegetal organism. Long and fierce were the controversies aroused by Liebig's views of the absorption of nitrogen from the air. Partisanship was keen; as a pupil of Hofmann I naturally studied the subject in connection with our food supply—and my interest continues to this day.

Our food depends on agriculture, and as the available wheat lands of the world inevitably contract, the economical cultivation of the soil becomes more and more a question of chemistry. At the Bristol meeting of the British Association in 1898 I re-opened the nitrogen question, not with a view to produce what has been called a "cosmic scare," but to show how by the application of known physical and chemical reactions, the shortage of fixed nitrogen, and consequently of wheat, can be overcome.

One of the first analyses I performed at the College of Chemistry was that of the mineral Cerite. The rare earths—my first, but not my only love—were then represented by ceria, lanthana, didymia, yttria, erbia, and terbia, and a specimen of yttria extracted from this cerite first gave me a key, thirty-three years later, to the citron band which then was haunting my laboratory.

Soon after Schrötter's discovery of amorphous phosphorus the great Professor came to the College of Chemistry to demonstrate to Hofmann the conversion of yellow phosphorus into the red variety. At that time I had acquired some skill in blowpipe manipulation, and was asked to help fit up the apparatus under Schrötter's directions.

The new art of Photography early attracted my attention. I remember the excitement caused by the announcement of Daguerre's and Fox Talbot's discoveries. I was working at photography in 1848, and not long after I had the privilege of being shown the Talbotype process by the Master himself. One of my most highly prized relics is a copy of Talbot's "Pencil of Nature." In these snap-shot days it may be of interest to remember that portraiture was an affair of minutes not seconds. I think there is one at least of my audience whom I victimised by a five-minute sitting in sunlight with his face chalked!

Niépce de St. Victor had discovered that Uranium salts possessed the property of storing up light and giving it out in the dark, and in 1858 I took what was perhaps the first radium photograph in this country, by writing with solution of uranium nitrate on a card, insolating it, and then putting it face to face in the dark with a sheet of photographic paper; the image of the writing was reproduced on the paper. Also among my earliest recollections in photography is a photograph of the solar spectrum in its true natural colours by Edmond Becquerel. Those who had the advantage of examining Becquerel's coloured photographs in their early perfection will agree with me that they hardly fell short of the recent productions of Lippmann.

I took some of the earliest stereoscopic photographs for Wheatstone, and in 1852 I commenced work on the photography of solar and metallic spectra—work which has increasingly fascinated me to the present day.

I cannot say I was present at the birth of the Daltonian atom—but it is not unlikely I shall see its deposition from the supreme place in chemical theory. The chemical

elements long have been considered to be manufactured articles, to use a phrase of Sir J. Herschel's, and as such they are subject to change and decay. They come into being and owe their stability to the outcome of a struggle for existence—a Darwinian development by chemical evolution. Just as in the biological world we have the survival of the fittest, so in the inorganic world we have the survival of the most stable or inert.

Hunting over some residues left after the preparation of selenium I was confronted with my first anomaly—a bright green line in the spectrum. This started me on the Thallium quest, and when determining the atomic weight of thallium I came to my second anomaly,—the behaviour of bodies in a vacuum balance. Following this clue I entered on the long research which culminated in the Radiometer. In the high vacua obtained in these researches many electrical eccentricities were encountered, and in the long struggle to arrive at an explanation, behold the phenomena of Radiant Matter! The action of radiant matter, or as we now say, of electrons on the rare earths caused some to glow with a phosphorescent light; on submitting this light to the scrutiny of the spectroscope another mystery—a bright citron coloured line in the spectrum of the glowing solid—clamoured for explanation. Hence the yttrium and samarium investigation, and then the scandium work on which I am now sedulously engaged. Incidentally, radiant matter opened the door to radio-activity, and nowadays radio-active bodies are bringing new elements to light with bewildering rapidity.

One of my closest friends in the early fifties was Robert Murray, an old man who in his younger days had been assistant to Davy in his lectures at the Royal Institution. He was with Davy during his most eventful discoveries, and I have had descriptions of the isolation of the alkali metals from an actual eyewitness.

I was early introduced to the Royal Institution by the Secretary, the Reverend John Barlow, my pupil at the Royal College of Chemistry. More than half a century of the Friday evening lectures means initiation into a whole cycle of wonders and mysteries wrested "From Nature's Inner Shrine." Interference of Light by Young, Potassium and Sodium by Davy, Liquefaction of Gases and Electricity from the Magnet by Faraday, Low Temperature work by Dewar, &c., &c. The list of scientific victories is endless.

Among the early speculations I heard propounded by Faraday were those on the nature of electricity and the ultimate constitution of matter. In the highly rarefied regions of present day speculation our progress is so rapid as to take away one's breath! It seems no Law is more certain than the Law of Change. A bit of Radium that would go into a thimble has almost suddenly shaken our belief in the conservation of substance, the stability of the chemical elements, the undulatory theory of light, and the nature of electricity; has revived the dream of the alchemists and the preservation of perpetual youth, and has cast doubts on the very existence of matter itself! For physicists are beginning to say that in all probability there is no such thing as Matter; that when we have caught and tamed the elusive atom and have split it into 700 little bits, these residual particles will turn out to be nothing more than superposed layers of positive and negative electricity.

For many years I have been connected with a War Department Committee, one of whose duties it is to investigate methods of killing the greatest number of one's fellow creatures in the shortest possible time. Researches of this character, Super-Dreadnoughts, big guns, cordite, and lyddite, are the greatest of all preservers of Peace.

What our country now most urgently requires are Researchers. We have any number of practical men, but Brain-Craft is the master of Hand-Craft. England needs Brain-Craft. We want men who cultivate Chemistry for its own sake without substratum of utilitarianism. Men whose discoveries, like that of phosphorus by Brandt, of the electric oxidation of nitrogen by Priestley, of potassium and sodium by Davy, of aniline by Unverdorben, of benzol by Faraday, and of chloroform by Soubeiran, seemed at the time never likely to be of the slightest use to anybody! With every man-slaying improvement our Committee elaborated I said to myself, "Another ten years' Peace for my country!" It is the truest economy to spend money without stint to keep all such enquiries and appliances at their highest possible efficiency, knowing that in this way only can Researchers be certain of securing the needful Peace, without which no serious investigations can be carried to a successful conclusion.

Modern enterprise demands that as soon as a machine ceases to work well it is best to scrap it. After sixty years of research work I begin to feel like a drone in a busy hive. But instead of ruthlessly consigning me to the scrap heap, my kind friends have dined me, have said most flattering things about me, and have warmed my heart.

I must again thank you not only for the honour you have paid me to-night, but for listening to the expression of thoughts that are perhaps more of personal than general interest. My experience has been long and varied, and when I contemplate the work I have tried to do in the time that has been allotted me, I am afraid I must echo the sentiment of the wise man of old:—"When a man has done, then he beginneth; and when he leaveth off, then shall he be doubtful."

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY

Ordinary Meeting, November 3, 1910.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Trypanosome Diseases of Domestic Animals in Uganda.* II. Trypanosoma Brucei (*Plimmer and Bradford*)." By Colonel Sir D. Bruce, C.B., F.R.S., and others.

"*Trypanosome Diseases of Domestic Animals in Uganda.* III. Trypanosoma vivax (*Ziemann*)." By Colonel Sir D. Bruce, C.B., F.R.S., and others.

"*Further Results of the Experimental Treatment of Trypanosomiasis; being a Progress Report to a Committee of the Royal Society.*" By H. G. Plimmer, F.R.S., W. B. Fry, and H. S. Ranken.

This Paper gives detailed results of the continuation of the work which has been going on under the direction of a Sub-Committee of the Royal Society.

The general results have confirmed an opinion which we have before expressed, viz., that antimony is a more powerful trypanocide than arsenic, and that such compounds as we have tried have not shown such severe toxic effects as some arsenic compounds have.

But there are unpleasant effects produced (varying according to the animal used) by antimony, such as sloughing and necrosis at the seat of injection and severe pain, so we have devoted considerable time to the study of new methods, and new forms of antimony. Finding that in dogs the subcutaneous and intramuscular administration caused pain, and sloughing of the tissues, intravenous injections of the salts were tried. The elimination of the antimony was so rapid, however, that, beyond prolonging life, little good effect was produced. So that eventually the injection of the metal itself, in state of finest division (devised and prepared for us by Dr. R. H. Aders Plimmer, of University College), was tried. This is taken up by the leucocytes, and is gradually transformed into some soluble compound, and our idea was that perchance it might be carried to parts of the body not easily accessible to other methods of administration.

The results so far have been on the whole more satisfactory than those of any other means we have tried, but the technique in many animals is difficult, and there have been difficulties in the preparation of the antimony.

Although putting a metal into the circulation sounds impossible, we have not had any case of plugging of capillaries in rats, guinea-pigs, rabbits, dogs, goats, or horses. It of course acts much more slowly than the salts, and takes from two to three times as long to clear the peripheral circulation of trypanosomers as subcutaneous injection of a salt does. But the excretion is also much slower, so that the blood and organs are in much longer contact with antimony than when a salt is administered. If carefully administered no irritation of the tissues is produced, and the vessel walls are not affected.

Animals appear to be more susceptible to overdosage than with the salts; and it is curious that an animal with trypanosomes in the blood can bear well a dose which is fatal to a healthy animal. It has also been used intraperitoneally, successfully in rats and rabbits.

A number of experiments have been made with silver salts, with negative results in every case. A number of experiments have been made with two new compounds (one an arsenic-camphor compound, one an organic antimony compound), kindly sent to us by Dr. Morgan, of the Imperial College of Science, with negative results.

Details of treatment of dogs, rabbits, goats, and horses are given in the paper.

"*Peculiar Morphology of a Trypanosome from a Case of Sleeping Sickness, and the Possibility of its being a New Species* (T. rhodesiense)." By J. W. W. STEPHENS, M.D., D.P.H., and H. B. FANTHAM, D.Sc., B.A.

"*Note upon the Examination, with Negative Results, of the Central Nervous System in a Case of Cured Human Trypanosomiasis.*" By FREDERICK W. MOTT, M.D., F.R.S.

"*Origin of the Hydrochloric Acid in the Gastric Tubules.*" By Miss M. P. FITZGERALD.

"*Fermentation of Galactose by Yeast and Yeast Juice.*" (Preliminary Communication). By A. HARDEN, M.D., F.R.S., and R. V. NORRIS.

"*Opposite Electrification produced by Animal and Vegetable Life.*" By W. M. THORNTON.

"*Remarkable Pharetronid Sponge from Christmas Island.*" By R. KIRKPATRICK.

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

Ordinary Meeting, November 7, 1910.

Mr. E. GRANT HOOPER in the Chair.

"*The Relation of Chemical Industry to Metallurgy.*" By ARTHUR C. CLAUDET.

In order to effect improvements in old processes or bring new ones to success, considerable chemical and metallurgical knowledge is necessary, especially as the economy of a process must always be considered; in fact, it may be better to sacrifice a large percentage of extraction for a lower one, if by the latter greater profits can be made.

For many years chemical industry and metallurgy were widely separated, but at the present time their boundaries may be regarded as having met and to a large extent overlapped. It is therefore highly desirable that the members of these two great industries should become more intimately associated than they are at present, so that the most rapid progress may be made and the greatest value obtained from each. The composite science of metallurgy—especially in regard to several of the non-ferrous metals—might have developed still more rapidly during the last thirty years, had its practitioners kept more closely in touch with the rapid progression of industrial chemistry during this period. It must not be lost to sight, moreover, that both sciences are very dependent on a third—mechanical engineering—as in many cases the greatest difficulty incurred in working out a process is of a mechanical nature.

The utilisation of by-products from smelting processes occupies the attention of the chemist much more than formerly. Selenium, tellurium, bismuth, gold, and silver, which are often present in copper ores, are now collected as valuable residues during the electrolytic refining of blister copper, and after separation are made valuable. Arsenic is collected from the flues of smelting furnaces, and is a valuable by-product, especially in the calcination of Cornish tin-ores. Coke-ovens and blast-furnace gases yield by-products of great value, such as ammonium sulphate. The success of the shale-oil industry depends largely upon the profits derivable from the ammonium sulphate by-product. Blast-furnace gases are utilised as a source of energy and for the manufacture of sulphuric acid. Basic phosphatic slag from the iron furnaces is a valuable fertiliser, and in certain cases is worth as much as the iron itself. Some iron slags are utilised to make cement.

Electric smelting, if brought to a successful issue, seems likely to alter considerably the position of many metallurgical industries. One example is the work now being carried out in Norway and Sweden, where power is cheap, on zinc-ores and concentrates.

The following ore treatment processes are described as demonstrating the relation of chemical industry to metallurgy:—

1. The cementation process carried out at mines operated in Southern Spain or cupriferous pyrites, such as at Rio Tinto, Tharsis, San Domingos (Portugal), &c.
2. The treatment of Spanish cupreous iron pyrites imported direct to Great Britain and other European countries for sulphur and copper extraction.
3. Pyritic smelting.
4. Another instance of the chemist and the metallurgist being together concerned in the beneficial treatment of ores is the case of the well known Broken-Hill lead-zinc-silver sulphide ores.
5. The manufacture of sulphate of copper. At first sight this would seem to be a chemical process, pure and simple; but on looking into it various metallurgical operations are found to play a part in the process.
6. The Pearce process of treating auriferous copper was the product of both chemist and metallurgist.
7. The arsenical cobalt and nickel silver ores now being mined in Ontario afford an interesting field for research work for the chemist and the metallurgist. These ores are very rich in silver, often yielding several thousands of ounces to the ton. Great difficulties have been met with in their satisfactory treatment; arsenic may reach up to 30 per cent, cobalt and nickel 10 to 15 per cent in each case. Efforts have been made to save not only the silver, but also the cobalt, nickel, and arsenic.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, November 2nd, 1910.

Mr. E. W. VOELCKER, President, in the Chair.

MR. Robert William Clarke was elected a Member of the Society.

Certificates were read for the first time in favour of Messrs. Claude L. L. Claremont, 62, Albert Street, Regent's Park, N.W.; and Harold Douglas Elkington, St. Aubyns, Woodborough Road, Putney.

Certificates were read for the second time in favour of Messrs. Gunner Jörgensen and Frederick Farey Shelley.

The following papers were read and discussed:—

"*Estimation of Lactose in the presence of commonly occurring Sugars.*" By JULIAN L. BAKER and H. F. E. HULTON.

The direct estimation by chemical methods of lactose in presence of other sugars which reduce alkaline copper salts and rotate the plane of polarised light presents considerable difficulties and in some mixtures is obviously impracticable. The authors have shown that lactose is unfermented by ordinary brewers' yeast, and on this they have based a method which permits of 97 to 100 per cent of the lactose present being found. The method is particularly useful for the estimation of lactose in certain types of infants' and invalids' foods.

"*Colorimetric Estimation of Hydrogen Cyanide.*" By A. Chaston Chapman.

In continuation of his work on the nature of the Jaffé reaction, the author has studied the action of hydrogen cyanide on the alkaline picrate solution. It is almost invariably stated that in this reaction potassium isopurpurate (the potassium salt of dicyano-picramic acid) is formed, and such is the case when the cyanide in excess is allowed to act upon a faintly alkaline solution of potassium picrate at a suitable temperature. Under the conditions, however, in which the process is usually employed as a test for cyanides, it is found that the action is one of reduction, the alkaline salts of the amino-nitro phenols, and not the isopurpurate, being formed. Under these circumstances it will be seen that the reaction is of very little value as a test for hydrogen cyanide, since almost any reducing substance will give the same result. Under well defined conditions the reduction of the picrate may be used for the colorimetric estimation of small quantities of hydrogen cyanide, but since acetone, aldehyde, hydrogen sulphide, and other volatile substances are capable of reducing the picrate, it is clear that the method can only have a very limited sphere of usefulness in toxicological practice. The author describes the conditions under which the best results can be obtained in the colorimetric estimation of hydrogen cyanide, but points out that the analyst must in all cases assure himself that any coloration he may obtain is due to hydrogen cyanide, and not to any other reducing substance.

"*Polarimetric Estimation of Milk Sugar.*" By H. Droop Richmond.

Acid mercuric nitrate does not precipitate the whole of the (lævo-rotatory) proteins of milk, and further amounts are removed by the addition of phospho-tungstic acid. Polarisation of the filtrate from phospho-tungstic acid yields results slightly higher with ordinary milk, and from 1 to 3 per cent higher with dried milk preparations.

"*New Method of Estimating Phosphoric Acid.*" By G. F. Wesley Martin.

The phosphoric acid is precipitated as ammonium phosphomolybdate. The precipitate, after being washed with distilled water, is dissolved in an excess of caustic alkali, and the ammonia distilled over into a measured quantity of standard acid: 102 parts NH_3 = 142 parts P_2O_5.

CHEMICAL SOCIETY.

(Continued from p. 243).

221. "*The Oxidation of Monohydric Phenols with Hydrogen Peroxide.*" By George Gerald Henderson and Robert Boyd. (*Trans.*, 1910, 1659).

A 30 per cent aqueous solution of hydrogen peroxide has been found to be a good oxidising agent for monohydric phenols of the benzene series, the products being either a dihydric phenol, or a quinone, or even in some cases a tetrahydric phenol. From the results obtained with a number of phenols, it appears that those monohydric phenols in which the para-position relative to the hydroxyl group is unoccupied are most easily attacked by the oxidising agent, and yield as the main product either a *p*-dihydric phenol or a quinone according to the conditions of the experiment. On the other hand, those monohydric phenols in which the para-position relative to the hydroxyl group is occupied are not so easily oxidised, and usually yield dihydric phenols in which the hydroxyl groups are in the ortho-position to each other. Several new compounds were obtained.

Some experiments on the action of hydrogen peroxide on cyclic hydrocarbons were also made. The hydrocarbons of the benzene series which were examined appeared to be somewhat indifferent to the action of the oxidising agent, but naphthalene, anthracene, and phenanthrene were readily attacked, yielding phthalic acid, anthraquinone, and phenanthraquinone respectively.

222. "*Solubilities of Organic Substances in Organic Solvents, a Contribution to the Theory of Solubility.*" By Dan Tyrer. (*Trans.*, 1910, 1778).

The solubility of a substance in a particular solvent is governed by two factors, namely, (1) the temperature, and (2) the concentration of the solvent, or the amount of solvent in unit volume of the saturated solution. Expressed mathematically, the solubility of a solute in a particular solvent under all possible conditions is given by the equation $S = K.f(C).\phi(T)$, where S is the solubility, C the concentration of the solvent, T the temperature, and K a constant. The object of the work was to determine the form of the function $f(C)$.

In order to avoid complications arising from the existence or formation of associated molecules in the solutions, the solubility of organic substances in organic solvents was studied. These were chosen also so as not to contain hydroxyl, amino-, or cyanogen groups in order to minimise the possible formation of associated molecules. The method of attacking the problem was to find a solute soluble in a solvent A and insoluble in another solvent B, which is miscible with A in all proportions. The solubility of the solute in the mixed solvent is then determined, and the results are plotted against the concentration of the solvent in the saturated solution. Whilst some of the cases investigated give results which approximately represent the solubility at constant temperature as a linear function of the solvent concentration, the general conclusion deduced from the results is that no simple and common law governs the relation between the solubility and the concentration of the solvent.

Incidentally, determinations of the solubility of some organic substances in organic solvents were made at varying temperatures, and also of the concentrations of the solvents in the saturated solutions. It was noticed that in all the cases investigated the concentration of the solvent could be very approximately represented as a linear function of the temperature.

223. "*The Chlorination of Toluene.*" By Julius Berend Cohen, Harry Medforth Dawson, John Reginald Blockey, and Arnold Woodmansey. (*Trans.*, 1910, 1623).

Experiments have been made to determine the influence of various factors on the relative proportions of benzyl chloride and of *o*- and *p*-chlorotoluenes, which are obtained in the chlorination of toluene. The results indicate that side-chain substitution is favoured by light and by rise of temperature, whereas nuclear substitution is favoured by the presence of small quantities of water and by adding to the toluene substances like nitrobenzene, which tend to promote the formation of polyhalogen compounds. Electrolytic chlorine behaves practically the same as ordinary chlorine.

In respect of the above-mentioned factors, the chlorination process appears to be influenced in the same way as the bromination process, and the view is adopted that side-chain substitution is effected by halogen molecules, whereas nuclear substitution is brought about by halogen which is combined with the halogen acid in the form of polyhalogen compounds. This theory has already been put forward by Hollemann (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, viii., 512; *Rec. Trav. Chim.*, 1908, xxvii., 435) to account for observations relating to the action of bromine on toluene.

A method for the analysis of mixtures of toluene, benzyl chloride, *o*-chlorotoluene, and *p*-chlorotoluene is described.

224. "*The Constitution of the Benzenetetracarboxylic Acids.*" By HANNAH BAMFORD and JOHN LIONEL SIMONSEN. (*Trans.*, 1910, 1904).

A synthesis of Baeyer's mellophanic acid from 1 : 4-dimethylnaphthalene is described, and proof is adduced that the usual views on the constitution of mellophanic and prehnitic acids are incorrect. Prehnitic acid is 1 : 2 : 3 : 5-benzenetetracarboxylic acid, whilst mellophanic acid is the corresponding 1 : 2 : 3 : 4-compound.

225. "*Action of Light on the Stereoisomeric Piperonylideneacetones and on other Unsaturated Ketones.*" By HANS STOBBE and FORSYTH JAMES WILSON. (*Trans.*, 1910, 1722).

The authors have recently shown (*Annalen*, 1910, cccIxxiv., 237) that stereoisomeric ketones of the benzylidenedeoxybenzoin type, Ar·CH:CPh·COPh, can be converted into one another by the action of heat, small quantities of hydrochloric acid, or by direct sunlight, a state of equilibrium resulting. The two stereoisomeric piperonylideneacetones, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3$ (Haber, *Ber.*, 1891, xxiv., 618), have been investigated along similar lines, and similar results obtained.

It was next attempted to obtain the hitherto unknown stereoisomerides of anisylideneacetone, piperonylideneacetophenone, anisylideneacetophenone, and *o*-methoxybenzylideneacetophenone, but the experiments were unsuccessful. *Phenyl o-methoxystyryl ketone*, $MeO{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COPh$, was obtained by condensing *o*-methoxybenzaldehyde and acetophenone by means of sodium hydroxide in alcoholic solution.

Doubly unsaturated ketones of the type of cinnamylideneacetophenone, CHPh:CH·CH:CH·COPh, are, by the action of sunlight converted, not only into stereoisomerides but also into polymerides.

226. "cyclo*Hexane, its Separation from, and its Estimation in, Mixtures containing Benzene.*" By THOMAS STEWART PATTERSON and ALEXANDER FLECK. (*Trans.*, 1910, 1773).

A mixture of *cyclo*hexane and benzene may be separated by shaking with a small amount of ethyl tartrate, when the mixture separates into two layers. When a larger quantity of ethyl tartrate is added to the mixture a homogeneous solution results, and from the rotatory power of this the composition of the mixture can be determined by comparing the found rotatory power with that of mixtures of known composition.

227. "*The Vapour Pressures and Molecular Volumes of the Mercuric Halides and the Relations between Atomic Volumes of Elements before and after Combination.*" By EDMUND BRYDGES RUDHALL PRIDEAUX.

The vapour pressures of the liquid compounds from their melting-points to their boiling-points have been determined. The temperatures of equal vapour pressures were compared with those of fluorobenzene by Ramsay and Young's method. If in the equation,—

$$\frac{T'_A}{T'_B} = \frac{T_A}{T_B} + c(T'_B - T_B),$$

T_B and T'_B are the temperatures of fluorobenzene, $c(HgCl_2 = 0{\cdot}0005$, $c(HgBr_2) = 0{\cdot}00037$, and $c(HgI_2) = 0{\cdot}00025$. Trouton's constant for the boiling-point under 760 mm. pressure was found to be—

$HgCl_2$, 24·1; $HgBr_2$, 23·9; HgI_2, 23·7.

The specific volumes of the liquids were measured in silica dilatometers—the expansion being represented by the following, where D_t = density at $t°$:—

$HgCl_2$ (280—335°); $D_t = 4{\cdot}400 - 0{\cdot}002218\ (t - 280°)$.
$HgBr_2$ (240—340°); $D_t = 5{\cdot}116 - 0{\cdot}00338\ (t - 240°)$.
HgI_2 (255—355°); $D_t = 5{\cdot}238 - 0{\cdot}00322\ (t - 255°)$.

The ratios between the molecular volumes of the liquid compounds and the sums of the atomic volumes of the liquid elements, all measured at equal pressures of saturated vapour, are constant over the range of pressures investigated. These ratios are probably much the same as the ratios of the volumes of the atoms before and after combination. There is a slight expansion on combination which, stated as the percentage increase on the volumes of the elements, is equal to :—

For $HgCl_2$, 1·8; $HgBr_2$, 7·4; HgI_2, 9·5.

The numerical values of Trouton's constant and the expansions of the liquids show a slight association, diminishing in the order :—Chloride → bromide → iodide.

228. "*A Study of some Unsaturated Compounds containing the* tert.*-Butyryl Group.*" (Part I.). By ALFRED ARCHIBALD BOON and FORSYTH JAMES WILSON. (*Trans.*, 1910, 1751).

The authors have investigated the action of bromine on *piperonylidenepinacoline*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CO{\cdot}CMe_3$. This compound melts at 94 – 95°, and was obtained by the condensation of piperonal with pinacoline by means of sodium hydroxide. It gives an *oxime* (m. p. 144—145°), and, in chloroform solution, yields a *monobromide* (m. p. 110—111°), $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}CBr{\cdot}CO{\cdot}CMe_3$ (*α*-compound), or $CH_2{:}O_2{:}C_6H_3{\cdot}CBr{:}CH{\cdot}CO{\cdot}CMe_3$ (*β*-compound), and also a *dibromide*, $CH_2{:}O_2{:}C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}CO{\cdot}CMe_3$, which melts at 138 – 139°, and is the chief product of the reaction.

When absolute alcohol was allowed to act on the latter, a substance was obtained identical with that produced when the dibromide, in alcoholic solution, was treated with potassium hydroxide (1 mol.). This product, which melts at 82—83°, may be represented either as $CH_2{:}O_2{:}C_6H_3{\cdot}CHBr{\cdot}CH(OEt){\cdot}CO{\cdot}CMe_3$ (*α*) or $CH_2{:}O_2{:}C_6H_3{\cdot}CH(OEt){\cdot}CHBr{\cdot}CO{\cdot}CMe_3$ (*β*).

As a result of the action of potassium hydroxide (2 mols.) on the dibromide (m. p. 138—139°) in alcoholic solution, the authors obtained a compound identical with that already referred to, melting at 82—83°, and two ethoxy-derivatives of piperonylidenepinacoline,—

$CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}C(OEt){\cdot}CO{\cdot}CMe_3$ (*α*)

and $CH_2{:}O_2{:}C_6H_3{\cdot}C(OEt){:}CH{\cdot}CO{\cdot}CMe_3$ (*β*), melting at 86—87° and 112—113° respectively. These compounds may, however, be stereoisomeric.

229. "*A New Method for the Preparation of Aryl Ethers of Glycerol α-Monochlorohydrin.*" By DAVID RUNCIMAN BOYD and ERNEST ROBERT MARLE. (*Trans.*, 1910, 1788).

The aryl ethers of glycerol α-monochlorohydrin are conveniently prepared by leaving a mixture of the phenol, epichlorohydrin, and a small quantity of sodium hydroxide for some days at the ordinary temperature. *γ-Chloro-β-hydroxy-α-o-tolyloxypropane* (b. p. 166°/18 mm.) and the corresponding *p*-tolyl compound (b. p. 165°/14 mm.) have been prepared. The phenylurethane of *γ-chloro-β-hydroxy-α-phenoxypropane* melts at 70°, and the phenylurethanes of the *o-tolyloxy* and *p-tolyloxy*-compounds at 80—81° and 113 114° respectively.

230. "*The Action of Ammonia on the Glycide Aryl Ethers.* Part II. *Phenoxypropanolamines.*" By DAVID RUNCIMAN BOYD. (*Trans.*, 1910, 1791).

The constitution previously assigned to the primary base derived from *o*-tolyl glycide ether,—

$C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NH_2$,

has been confirmed by the preparation of the same substance from *γ*-chloro-*β*-hydroxy-*α*-*o*-tolyloxypropane and ammonia.

Phenyl glycide ether, when treated with a solution of ammonia in 50 per cent alcohol, gives a primary *base*, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NH_2$ (m. p. 97—98°), and a secondary *base*, $[C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2]_2NH$ (m. p. 101—102°).

231. "*The Relation of Position Isomerism to Optical Activity.* Part VIII. *The Rotation of the Menthyl Esters*

of the Alkyloxy- and Alkylamino-derivatives of Benzoic Acid." By Julius Berend Cohen and Harold Ward Dudley. (*Trans.*, 1910, 1732).

The present investigation is a continuation of former studies on the same subject, and deals with substituted menthyl benzoates containing positive in place of negative groups. Ten series of isomeric esters have been prepared, and their rotational values ascertained. The authors find that temperature is an important factor in such determinations. Whilst the temperature-coefficient for the ortho-compounds is small and in nearly all cases positive, that of the para-compounds is large and negative, the intermediate meta-compounds being small and also negative. It follows that if a comparison of the three isomerides is made at 100° instead of 20°, the rotational values of the meta- and para-isomerides approximate to that of the unsubstituted menthyl benzoate at the same temperature, whereas the value of the ortho-compound is widely divergent. The general rule which was previously established in the case of the halogen, nitro-, and nitro-halogen derivatives applies with equal truth to the menthyl esters containing positive groups, namely, *the ortho-substituent exerts a preponderating effect on the rotational value of the active group.*

232. "*The Volatile Constituents of Coal.*" By Maurice John Burgess and Richard Vernon Wheeler. (*Trans.*, 1910, 1917).

It is shown that with all coals, whether bituminous, semi-bituminous, or anthracitic, there is a well-defined decomposition-point at a temperature lying between 700° and 800°, which corresponds with a marked increase in the quantity of hydrogen evolved. With bituminous coals, the increase in the quantity of hydrogen evolved falls off at temperatures above 900°, but with anthracitic coals it is maintained up to 1100°.

It is further shown that ethane, propane, and butane, and, probably, higher members of the paraffin series of hydrocarbons, form a large percentage of the gases evolved at low temperatures, but that at temperatures above 700° the evolution of such hydrocarbons practically ceases.

The suggestion is advanced that coal of whatever geological age contains a compound which undergoes decomposition at temperatures above 700° (under the atmospheric pressure), and yields hydrogen as its principal gaseous product. It seems probable, also, that the same compound is responsible for the hydrocarbons of the paraffin series that make their appearance at low temperatures.

233. "*Tetramethyl Ferrocyanide and some Derivatives.*" By Ernald George Justinian Hartley. (*Trans.*, 1910, 1725).

Experiments have been made in continuation of the work recently published (*Trans.*, 1910, xcvii., 1066) on the reaction between potassium ferrocyanide and methyl sulphate.

By taking care to exclude moisture as far as possible, the reaction followed a somewhat different course, and a neutral *methyl sulphate*, $(CH_3)_6FeC_6N_6(CH_3{\cdot}SO_4)_2$, was isolated of the same base, the acid salts of which had been previously obtained. Unlike the acid methyl sulphate, this salt does not undergo any change on keeping in a vacuum over sulphuric acid. In addition to this, there were formed some of the acid sulphate previously described and another neutral salt of the same base, probably the ethyl sulphate. The neutral sulphate, $(CH_3)_6FeC_6N_6SO_4$, can be prepared from the acid sulphate by neutralising with barium hydroxide in aqueous solution, removing barium sulphate, and evaporating the filtrate in a vaccum. It is an unstable substance, differing from the acid salt in being soluble in ethyl alcohol. The corresponding chloride is prepared by neutralising with barium hydroxide as above, and then adding excess of barium chloride and evaporating to dryness. The salt is extracted from the excess of barium chloride with alcohol, and precipitated with ether. It is far more stable than the sulphate.

On heating the chloride under diminished pressure to 140°, methyl chloride is given off quantitatively, and almost pure tetramethyl ferrocyanide is left. This resembles the corresponding ethyl compound prepared from silver ferrocyanide and ethyl iodide in being soluble in chloroform and water, and giving in aqueous solution a white precipitate with mercuric chloride and a reddish purple coloration with ferric chloride. It is deposited from chloroform in well-formed crystals containing chloroform of crystallisation.

234. "*The Molecular Complexity of Amides in various Solvents.*" (Part II.) By Andrew Norman Meldrum and William Ernest Stephen Turner. (*Trans.*, 1910, 1605).

In continuation of their previous work (*Trans.*, 1908, xciii., 876) the authors have determined the molecular complexity of seventeen additional amides in the same organic solvents as before. The principal object of the work was to test the Nernst-Thomson hypothesis, that association of the solute tends to be high when the dielectric constant of the solvent is low, and *vice versa*. They regard their results as in good agreement with the hypothesis. The following table summarises the results (for organic solvents) of both investigations, and includes the dielectric constants of the solvents :—

Solvent.	Number of amides investigated.	Number of amides which form simple molecules.	Number of amides which form associated molecules.	Dielectric constant.
Alcohol ..	28	24	1 and 3 doubtful	25·4 at 18·5°
Acetone ..	27	20	4 and 3 doubtful	21·2 at 22°
Chloroform	22	3 and 1 doubtful	18	5 at 22°
Ether . ..	14	3 and 2 doubtful	9	4·4 at 18°
Benzene ..	21	3 and 1 doubtful	17	2·3 at 18°

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift für Anorganische Chemie. Vol. lxviii., No. 2, 1910.

Ternary Alloys of Magnesium, Zinc, and Cadmium. —G. Bruni, C. Sandonnini, and E. Quercigh. — The authors first investigated the two binary systems, Zn + Cd and Zn + $MgZn_2$; in the former case they obtained results agreeing very well with those of Hinrichs, except that the eutectic temperature appears to be 262° instead of 270°, and there was no indication of the formation of mixed crystals in alloys rich in cadmium. The solidification diagram of the system Cd + $MgZn_2$ was then determined, and finally the ternary diagram of the system Zn + Cd + $MgZn_2$. The compound Cd + $MgZn_2$ behaves like a single metal.

Chemical Composition of Stassfurth Salt Deposit. —Wilhelm Biltz.—In this paper the author publishes the results of the complete analysis of specimens of the potash deposits of Stassfurth, thus amplifying Precht's work on the subject.

Aryl and Alkyl Compounds of Tin.—P. Pfeiffer.—Tetra-*p*-tolyl tin, which has not previously been described, can very readily be prepared by the action of toluene magnesium bromide on tin tetrabromide. Its melting-point is

230°, *i.e.*, between that of tetratolyl silicon and tetratolyl lead. The tribenzyl tin compounds show a striking resemblance to the corresponding compounds in the silicon series both as regards their melting-points and from a chemical point of view. Methyl iodide reacts with an alcoholic alkaline solution of stannous oxide to give potassium methyl stannite at the ordinary temperature: $SnO_2K_2 + CH_3I = CH_3.SnO_2K + KI$. At the temperature of the water-bath the methyl stannite decomposes: $2CH_3.SnO_2K = (CH_3)_2SnO + K_2SnO_3$. Methyl stannous acid can be isolated by saturating an alcoholic solution of its potassium salt with carbon dioxide, and then driving off the alcohol on the water-bath. As a by-product of this reaction methyl stannoyl potassium carbonate is obtained, $CH_3.Sn\overset{O}{\leq}_{O.CO.OK}$. The homologues of methyl iodide —ethyl, propyl, tolyl iodide, &c.—react similarly with potassium stannite, but the corresponding alkyl stannous acids have not been isolated. Dibutyl tin compounds have been prepared by the author for the first time, and the dimethyl tin haloids have been thoroughly investigated. The following table gives the most important compounds with their melting-points:—$SnCl_4$ (33°), $SnBr_4$ (30°), SnI_4 (143°), CH_3SnCl_3 (43°), CH_3SnBr_3 (53°), CH_3SnI_3 (86·5°), $(CH_3)_2SnCl_2$ (108°), $(CH_3)_2SnBr_2$ (78°), $(CH_3)_2SnI_2$ (43°), $(C_2H_5)_2SnCl_2$ (84 — 85°), $(C_2H_5)_2SnBr_2$ (63°), $(C_2H_5)_2SnI_2$ (44°), $(C_3H_7)_2SnCl_2$ (81°), $(C_3H_7)_2SnBr_2$ (49°), $(C_3H_7)_2SnI_2$ (< −15°), $(C_4H_9)_2SnCl_2$ (43°), $(C_4H_9)_2SnBr_2$ (20°), iso$(C_5H_{11})_2SnCl_2$ (28°), iso$(C_5H_{11})_2SnBr_2$ (−2° to −4°).

Electrical Conductivity and Hardness of Silver-copper Alloys.—N. Kurnakow, N. Puschin, and N. Senkowsky.—It has been observed that the conductivities of some alloys of silver and copper of the same composition are very different, and to explain these deviations the authors have studied the conductivity of various alloys. Apparently alterations in the internal condition of a solid due to the technical processes used in working up the metal influence the conductivity, and when the metal is converted into the hard state a decrease of conductivity is observed. Heating also affects the conductivity. The investigation of the hardness of the Cu—Ag system confirms these results.

Spark Phenomena at the Electrodes during the Electrolysis of Fused Salts.—A. Kailan.—The anodic disturbance observed during the electrolysis of fused lithium chloride is not due to the formation of a subchloride; it is prevented by raising the temperature, and it seems possible that the phenomenon is connected with some change in the viscosity. The apparent resistance of the cell decreases with increasing tension as long as the phenomenon occurs. A mixture of one part of lithium bromide and six parts of lithium chloride gives the same results, but less easily than when the pure chloride or a mixture of the chloride and potassium chloride is used.

Preparation of Manganic Fluorides and Titration of Manganese in presence of Fluorides.—Erich Müller and Paul Koppe.—The red potassium manganese fluoride $2KF.MnF_3.H_2O$ can be prepared by mixing permanganate, manganous sulphate, and hydrofluoric acid in the proportions given by the equation $MnO_4' + 4Mn'' + 8H' = 5Mn''' + 4H_2O$, and adding the corresponding amount of potassium fluoride. The above equation suggests that manganese could be titrated with permanganate in presence of hydrofluoric acid, but the end of the reaction cannot be determined with sufficient accuracy. Volhard's method of determining manganese in presence of fluorides gives incorrect results.

Equilibrium in the Action of Caustic Potash on Mercury Bromide and Chloride.—W. Herz.—The equilibrium equation of the action of caustic potash on $HgBr_2$ is $HgBr_2 + 2KOH \rightleftharpoons HgO + 2KBr + H_2O$. The results of the calculation of the constants of the law of mass action agreed very well among themselves in the different experiments and fairly well with those of Bugarszky's experiments.

MISCELLANEOUS.

Conference on Chocolate and Cocoa.—At the International Food Congress which was held in Paris in 1909 there were many discussions on the subject of what should constitute purity in cocoa and chocolates, but the findings of the Congress were not universally accepted. Consequently a strong desire has arisen for a special Congress in connection with the subject, and it has been arranged that such should take place in Paris in January, 1911, when there will be present delegates from Germany, England, Austria, Hungary, Belgium, Brazil, Spain, the United States, France, Holland, Italy, Mexico, and Switzerland. The Congress will be limited to five representatives from each nation, but each nation will only have the right to one vote, so that the delegates must arrange beforehand how their votes will be given. The Congress is being arranged under the auspices of the White Cross Society of Geneva, whose delegate in the United Kingdom is Mr. Loudon M. Douglas, F.R.S.E., of 3, Lauder Road, Edinburgh.

Andrew Carnegie Research Scholarship.—A Research Scholarship or Scholarships, of such value as may appear expedient to the Council of the Iron and Steel Institute from time to time founded by Mr. Andrew Carnegie (Past-President), who has presented to the Iron and Steel Institute eighty-nine $1000 5 per cent Debenture Bonds for the purpose, will be awarded annually, irrespective of sex or nationality, on the recommendation of the Council of the Institute. Candidates, who must be under thirty-five years of age, must apply on a special form before the end of February to the Secretary of the Institute. The object of this scheme of Scholarships is not to facilitate ordinary collegiate studies, but to enable students who have passed through a college curriculum or have been trained in industrial establishments, to conduct researches in the metallurgy of iron and steel and allied subjects, with the view of aiding its advance or its application to industry. There is no restriction as to the place of research which may be selected, whether university, technical school, or works, provided it be properly equipped for the prosecution of metallurgical investigations. The appointment to a Scholarship shall be for one year, but the Council may at their discretion renew the Scholarship for a further period instead of proceeding to a new election. The results of the research shall be communicated to the Iron and Steel Institute in the form of a paper to be submitted to the Annual General Meeting of members, and if the Council consider the paper to be of sufficient merit, the Andrew Carnegie Gold Medal shall be awarded to its author. Should the paper in any year not be of sufficient merit, the Medal will not be awarded in that year.

MEETINGS FOR THE WEEK.

Monday, 21st.—Royal Society of Arts, 8. (Cantor Lecture). "Industrial Pyrometry," by C. R. Darling.

Wednesday, 23rd.—Royal Society of Arts, 8. "Methods of Detecting Fire-damp in Mines," by Sir Henry H. Cunynghame, K.C.B.

Thursday, 24th.—Royal Society. "Colour Blindness and the Trichromatic Theory—Part II., Incomplete Red or Green Blindness," by Sir W. de W. Abney. "Sequence of Chemical Forms in Stellar Spectra," by Sir Norman Lockyer. "Influence of Viscosity on the Stability of the Flow of Fluids," by A. Mallock. "An Electrostatic Voltmeter for Photographic Recording of the Atmospheric Potential," by G. W. Walker. "Optical Dispersion—An Analysis of its Actual Dependence upon Physical Conditions," by Dr. T. H. Havelock. "Spectrum of Halley's Comet," by C. P. Butler.

Friday, 25th.—Physical, 5. "Electric Stress at which Ionisation begins in Air," by Dr. A. Russell. "After-glow produced in Gases by Electric Discharge," by Prof. the Hon. R. J. Strutt. Exhibition of a Surface Brightness Photometer, by J. S. Dow. "Approximate Solution of various Boundary Problems by Surface Integration combined with Freehand Graphs," by L. F. Richardson.

THE CHEMICAL NEWS.

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REPORT ON GASEOUS COMBUSTION.*

By WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S.

This report aims at summarising the results of the principal researches upon the chemical aspects of gaseous combustion during the past thirty years.

Synopsis.

Introduction.—The earlier work of Davy and Bunsen. The latter's erroneous assumption of "discontinuity" in gaseous combustion. The new era inaugurated by the investigations of Mallard and Le Chatelier, Berthelot and Vieille, and of H. B. Dixon and H. B. Baker.

Section I. *Ignition Temperatures and the Initial Phases of Gaseous Explosions.*—Slow combustion below the ignition point. Recent determinations of ignition temperatures by H. B. Dixon and H. F. Coward. Rates of ignition. Photographic researches of Mallard and Le Chatelier and of H. B. Dixon and his pupils upon the initial phases of gaseous explosions and the influence of reflected compression waves in accelerating combustion and determining detonation. Discovery of "retonation" and its bearing upon the question of residual or continued combustion in gaseous explosions.

Section II. *The Explosion Wave.*—Discovery by Berthelot and Vieille of "detonation" (*l'onde explosive*) in gaseous explosions. Theories advanced by Berthelot, H. B. Dixon, and D. L. Chapman respecting rates of explosion. Influence of inert gases upon rates of explosion. Inferences to be drawn from observed rates of explosion respecting the combustion of gaseous carbon and of hydrocarbons.

Section III. *The Pressures produced in Gaseous Explosions.*—Experiments by Bunsen in 1867, by Mallard and Le Chatelier in 1883, and by Berthelot and Vieille in 1885. Discussion of the reasons why the maximum pressures ordinarily observed in gaseous explosions are always considerably less than those calculated on the supposition of adiabatic conditions and the constancy of the specific heats of the products. Evidences that (1) increases in the specific heats of steam and carbon dioxide with temperature, (2) continued combustion, and (3) loss of heat by direct radiation from explosion flames, affect the maximum pressures observed. Possible influence of dissociation.

Section IV. *The Influence of Moisture upon Combustion.*—Discovery by H. B. Dixon of the non-inflammability of a thoroughly dried mixture of carbon monoxide and oxygen. H. B. Baker's researches. Instances in which gaseous combustion is apparently independent of the presence of water vapour. Theories respecting the function of steam in combustion.

Section V. *The Combustion of Hydrocarbons.*—Disproof of the older ideas of *preferential combustion*, whether of hydrogen or of carbon. Theory of the intermediate formation of "oxygenated" or "hydroxylated" molecules in hydrocarbon combustion as suggested by the author's researches. Schemes representing the combustion of typical hydrocarbons. Presence of water vapour not essential in hydrocarbon combustion. Outward differences between the partial combustion of olefines and paraffins. The much greater affinities of hydrocarbons as compared with hydrogen or carbonic oxide for oxygen at high temperatures.

Section VI. *The Influence of Hot Surfaces upon Combustion.*—The earlier researches and theories of Davy, Dulong and Thénard, William Henry, Thomas Graham, Döbereiner, Fusinieri, Faraday, and De la Rive. Surfaces as accelerators of gaseous combustion. The factors operative in "surface combustion" as revealed by recent investigations. The "activation" of hydrogen by heated surfaces. The electrical condition of surfaces during surface combustion.

Introduction.

The era in the scientific investigation of gaseous combustion with which this Report is specially concerned was inaugurated some thirty years ago by the pioneering researches of the French savants Mallard and Le Chatelier, and M. Berthelot on the initial stages of "inflammation" and the setting up of "detonation" in explosive mixtures, and by the equally fruitful discoveries by H. B. Dixon and H. B. Baker concerning the part played by steam in combustion. Previous knowledge of the chemistry of fire had been mainly derived from the researches of Davy and his contemporaries (1815 to 1825), and those carried out or inspired by Bunsen some fifty years later. Davy's work, primarily undertaken in order to elucidate the causes of explosions in coal-mines, had disclosed and brought within range of experimental enquiry the broad facts connected with the ignition of explosive mixtures, the influence of narrow passages and of cold surfaces in extinguishing flames, the relative "combustibilities" and "explosion limits" of inflammable gases, and the effects of rarefaction and dilution upon gaseous combustion. Finally, his notable discovery of the flameless combustion of hydrogen and of coal-gas in contact with a glowing spiral of platinum, followed by the more systematic investigations of Dulong and Thénard, had drawn attention to the "intensifying" influence of hot surfaces upon combustion, the importance of which has perhaps never been fully appreciated.

But the work of Davy, standing as it does between the ages of Lavoisier and Clausius, and singularly fruitful as it was in its immediate practical results, gave rise to no great theoretical developments. Soon after his death, the path of progress became choked with error; there arose the dogma of the selective combustion of hydrogen in hydrocarbon flames, which, although inconsistent with Dalton's experiments on the partial combustion of ethylene and methane, continued to dominate chemical science for more than half a century. There is no evidence that Davy himself ever countenanced this doctrine, but it possibly may have been suggested to his immediate successors by his mistaken views concerning the much higher combustibility of hydrogen as compared with hydrocarbons—a notion which is still widely prevalent.

Bunsen's researches upon gaseous combustion, whilst they did incalculable service to chemistry and metallurgy in introducing exact methods of gas analysis and in elucidating the reducing action of carbon monoxide in the blast-furnace, unfortunately gave rise to certain misconceptions, due to unsuspected errors in the experimental methods employed. His experiments on the division of oxygen between carbon monoxide and hydrogen, which were originally undertaken to test the law of mass action, are now recognised to have been vitiated by the fact that he worked with undried gases in a "wet" eudiometer. From his results, however, he concluded that the condition of equilibrium in such a case is determined by an assumed tendency to form certain "hydrates of carbon dioxide," and undergoes discontinuous alteration on gradual change in the relative proportions of the combustible gases originally present. But whilst this conclusion was afterwards disproved by the independent researches of H. B. Dixon and Horstmann, the underlying notion of "discontinuity" or variation *per saltum* in regard to gaseous combustion is still occasionally met with in technical literature.

A similar error crept into Bunsen's interpretation of the results of his measurements of the pressures produced when either hydrogen or carbon monoxide is exploded with half its own volume of oxygen at atmospheric pressure in a closed vessel. He contended that, in either case, *one-third* only of the gases combine in the first instance, whereby

* Read before the British Association (Section B), Sheffield Meeting, 910.

the temperature of the system is raised to some point between 2844° and 3033°; that it then falls by radiation to 2558°, between which point and 1146° a further *one-sixth* of the mixture combines, leaving the remaining *half* to burn as the system cools down to the ordinary temperature. This idea of combustion *per saltum* was revived again by von Oettingen and von Gernet in 1888, in connection with their photographic researches on the explosion of electrolytic gas (*Ann. Phys. Chem.*, xxxiii., 586), but it has been clearly proved by H. B. Dixon that their observations can be explained on other grounds.

Bunsen's first measurements of the rates at which flames are propagated in gaseous mixtures (namely, 34 metres per second for a mixture $2H_2+O_2$, and 1 metre per second for a mixture $2CO+O_2$) have since been shown to apply only to the initial stages of an explosion, where the gases combine with relatively very slow velocities compared with those characteristic of "detonation." It was in the year 1881 that Berthelot, and independently Mallard and Le Chatelier, announced the discovery of the rapid acceleration of the initial velocity of inflammation and the final attainment of the enormously higher constant velocity of the "explosion wave."

SECTION I.—*Ignition Temperatures and the Initial Phases of Gaseous Explosions.*

Chemical change may be determined in a gaseous explosive mixture at a much lower temperature than its ignition-point. Thus, if electrolytic gas be heated in a sealed bulb to a temperature somewhat higher than 400°, the formation of steam can usually be detected after a lapse of a few days. Between 450° and 500° the rate of combination, although considerably greater, would still be insufficient to cause any self-heating of the mixture. If, however, the temperature of the enclosure be further slowly raised, a point (probably about 550°) would soon be reached at which self-heating of the mixture would begin; its temperature would thus be raised above that of the enclosure, and the rate of combination rapidly accelerated until explosive combustion would be set up. The precise temperature at which this would occur would obviously depend upon the amount of slow combustion which had taken place during the preliminary heating-up of the mixture. Thus it follows that the only way of determining the true ignition temperature of such a mixture, undiluted by the products of its own slow combustion, would be either to make the preliminary heating-up period negligibly short, or, better still, to heat separately the combustible gas and the air or oxygen to the ignition temperature before allowing them to mix.

The work of Victor Meyer and his pupils (*Ber.*, 1892, xxv., 622; 1893, xxvi., 2421 *Zeit. Phys. Chem.*, 1893, ii., 28), as also that of Hélier (*Ann. Chim. Phys.*, 1897, [7], x., 521) and Emich (*Monatsh.*, 1900, xxi., 1061), which yielded very discordant results for the ignition temperatures of mixtures of the commoner inflammable gases with oxygen, doubtless suffered from the large amount of flameless combustion which occurred before the temperature of the mixture as a whole had been raised to the true ignition-point.

Quite recently, however, H. B. Dixon and H. F. Coward (*Trans. Chem. Soc.*, 1909, xcv., 514), using an apparatus in which the combustible gas and air or oxygen were separately heated to the temperature of the enclosure before being allowed to mix, have succeeded in fixing, within narrow limits, the ignition temperatures at atmospheric pressure of a number of gases. In the cases of hydrogen, carbon monoxide, and acetylene, the ignition temperatures were practically the same in air as in oxygen, thus:—

	In air.	In oxygen.
Hydrogen	580—590°	580—590°
Carbon monoxide (moist)	644—658	637—658
Acetylene	406—440	416—440

In most other cases, however, the limiting temperatures observed in air were higher than in oxygen, thus:—

	In air.	In oxygen.
Methane	650—750°	556—700°
Ethylene	542—547	500—519
Cyanogen	850—862	803—818

Another notable fact is that in an homologous series of hydrocarbons the limiting ignition temperatures appear to fall as the series is ascended. Thus we have (in oxygen):—

Methane	556—700°
Ethane..	520—630°
Propane	490—570°

During 1906-7 K. G. Falk (*Journ. Am. Chem. Soc.*, xxviii., 1517; xxix., 1536), acting on a suggestion by Nernst, endeavoured to determine the ignition points of various mixtures of hydrogen and oxygen by compressing them in a steel cylinder by means of a weight falling on a piston. Assuming that (1) the mixture was heated adiabatically and uniformly throughout its whole mass until it reached the ignition-point, (2) that the whole then detonated instantaneously, and (3) that the downward movement of the piston was arrested at the moment of ignition, he calculated the ignition temperatures under adiabatic compression shown in the table given below.

H. B. Dixon (*Trans. Chem. Soc.*, 1910, xcvii., 674) in a recent criticism of Falk's assumptions, contends that whilst (1) may be in certain cases practically true, (2) and (3) cannot be allowed, and also that Falk's results are unreliable on account of his having neglected to stop the descent of the piston the moment the gases were brought to the true ignition-point. Adopting this necessary precaution, Dixon has repeated Falk's experiments, with results which compare as follows when δ is assumed to be 1·40 in all cases —

Mixture.	Ignition temperature under adiabatic compression.	
	Falk.	Dixon.
$4H_2+O_2$	605°	—
$2H_2+O_2$	540	536°
H_2+O_2	514	530
H_2+2O_2	530	520
H_2+4O_2	571	507

Using the specific heats of hydrogen and air found by Joly under high pressures, Dixon calculates the ignition-point of electrolytic gas to be 557° from his experiments on adiabatic compression. From Dixon's results it would also appear that successive additions of oxygen to electrolytic gas regularly lower the ignition-point.

We are principally indebted to the photographic researches of H. B. Dixon and his pupils (*Phil. Trans.*, 1903, Series A, cc., 315) for the most notable recent additions to our knowledge concerning the initial phases of explosion and the phenomena associated with the setting up of "detonation" in gaseous mixtures. The first investigators to use a photographic method were Mallard and Le Chatelier in their researches on the initial phases of gaseous explosions (*Annales des Mines*, viii., Series 4). They recorded the movement of the flame along a horizontal glass tube on a sensitised plate moving vertically, thus obtaining a graph compounded of the two velocities. Failing to obtain any satisfactory records with such feebly luminous flames as those yielded by mixtures either of carbon monoxide or of hydrogen with oxygen, they employed mixtures of carbon disulphide with either oxygen or nitric oxide, which they regarded as typical of all "oxygen" or "air" mixtures respectively.

The behaviour of these mixtures was found to differ according as they were ignited near (*a*) the *open* or (*b*) the *closed* end of a tube. In the case of (*a*) the flame proceeded for some distance down the tube at a practically uniform velocity, which is the true rate of propagation "by conduction"; with the mixture CS_2+6NO this state was succeeded by an oscillatory period, the flame swinging

backwards and forwards with increasing amplitudes, and then either dying out altogether or giving rise to "detonation"; with the oxygen mixtures the initial period of uniform slow velocity was shorter, and appeared to be abruptly succeeded by detonation without the intervention of any oscillatory period. When the nitric oxide mixtures were ignited near the *closed* end of the tube, the forward movement of the flame was uniformly accelerated until detonation was set up.

According to Le Chatelier the following numbers represent in *metres per second* the true initial rates of inflammation (*i.e.*, of the propagation of the flames "by conduction") for various mixtures:—

Hydrogen and Air.

Hydrogen (per cent).	Metres (per second.
10	0·60
20	1·95
30	3·30
40	4·37
50	3·45
60	2·30
70	1·10

Methane and Air.

Methane (per cent).	Metres (per second).
6	0·03
8	0·23
10	0·42
12	0·61
14	0·36
16	0·10

Acetylene and Air.

Acetylene (per cent).	Metres (per second)
2·9	0·1
5	2
7	4
9	6
15	3
22	0·4
40	0·22
60	0·07
64	0·05

Coal Gas and Air.

Gas (per cent).	Metres (per second).
8	0·30
10	0·50
12	0·72
14	0·93
15	1·05
17	1·27
20	0·80
24	0·40

Oxygen Mixtures.

$2CO+O_2$	2	metres pe second
$2H_2+O_2$	20	,,
CS_2+3O_2	22	,,
$C_2H_2+2\frac{1}{2}O_2$	200	,,

It should be noted that for mixtures of the same gas with various proportions of air, the initial rate of inflammation attains a maximum when the combustible gas is present in considerable excess of that required for perfect combustion.

H. B. Dixon's experimental method consisted in photographing the explosion flame travelling along a horizontal tube on a highly sensitive film rotated vertically with a constant high velocity (varying, however, between twenty-five and fifty metres per second in different experiments), the explosion tube being placed at such a distance from the camera that the size of the image was about one-thirtieth that of the flame. In this way it was found possible to analyse the progress of an explosion from its point of origin up to the final attainment of its maximum force and velocity in "*detonation*." The investigation also included the discovery of the wave of "*retonation*," which is thrown back through the still burning gases from the point where detonation starts (a phenomenon also independently discovered by Le Chatelier in 1900), of the effects of collision between two explosion waves, and of the passage of reflected waves through the hot products of explosion.

The phenomena associated with the development of an explosion in a gaseous mixture, fired in a closed tube by a spark passed between wires a few inches from the closed end, are very clearly shown in a photograph which is analysed in the diagram (Fig. 1). The photograph was

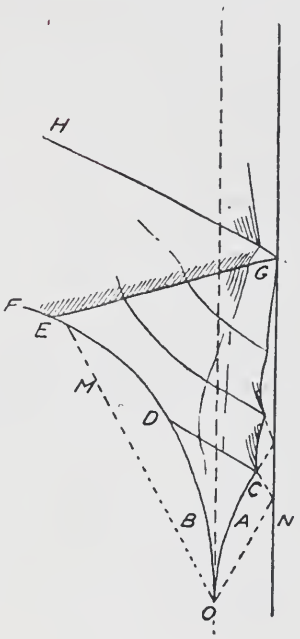

Fig. 1.

taken during an experiment in which carbon disulphide was exploded with a quantity of oxygen represented by the expression $CS_2 + 5O_2$. The flame, in starting at the point O, sends out invisible compression waves in both directions along the tube, which travel in advance of the flame with the velocity of sound through the unburnt gases, as represented by the dotted lines O M, O N in the diagram. The flame itself, travelling at first more slowly than the compression waves, traces the curves O A and O B. The compression wave O N, on reaching the closed end of the tube, is reflected back again as N C, and, on meeting the flame (which is still travelling in the direction O A), retards it, and passes thence through the hot and probably still burning gases as the visible wave C D. An instant later it overtakes at D the front of the flame, travelling in the direction O B, thereby accelerating it and increasing its luminosity in consequence of the quickened combustion. The flame then continues to move forward with rapidly accelerated velocity until "detonation" is set up at the point E. At this point a strongly luminous wave of compression E G (the "retonation wave") is sent backwards through the still burning gases, which, on reaching the near end of the tube, is reflected back again as G H. The "detonation wave" E F passes onwards through the mixture with its characteristic uniform high velocity and intense luminosity. A similar photograph shows the development of "detonation" and the phenomenon of "retonation" in the case of a mixture of cyanogen and oxygen ($C_2N_2+O_2$) fired near the closed end of a tube.

Except in special circumstances (*e.g.*, when it is reinforced by another reflected wave) the velocity of the retonation wave is always inferior to that of detonation; thus Le Chatelier gives 2990 metres per second for the "detonation wave" and 2330 metres per second for the "retonation wave" in an equimolecular mixture of acetylene and oxygen. When, however, the "retonation wave" is developed just at the closed end of a tube (*e.g.*, when the explosive mixture is fired at such a distance from the closed end that "detonation" is set up just as the flame arrives at the end) it may be reinforced by a reflected wave, in which case its velocity cannot be distinguished from that of a true "detonation."

The explanation of the intense luminosity of the retonation wave, and its higher velocity than sound through the exploded gases, is to be found in the fact that the combustion during the initial stages of an explosion is very much slower than when detonation is set up. Under the extreme conditions of "detonation" the temperature of each successive layer of the explosive mixture is suddenly raised to the ignition-point by adiabatic compression, and it is probable that a large proportion of collisions between chemically opposite molecules are fruitful of change. The whole combustion is probably completed in an immeasurably short interval of time, as the result of a comparatively limited number of successive molecular collisions. But during the initial period of the explosion ("inflammation") not only is the flame propagated with a much slower velocity, but also the actual process of combustion is much more prolonged than in detonation, and at the moment when detonation is set up combustion is still proceeding in the layers of gas for some distance behind the flame-front. The "retonation" wave, in passing backwards through these layers, quickens this residual combustion, and is itself thereby rendered highly luminous. This interpretation is supported by the repeated observations of Dixon that the collision of two flames, in neither of which "detonation" has been determined, will frequently give rise to reflected waves more rapid and more luminous than the incident waves. There can be little doubt as to the important part played by reflected waves in determining the violent shattering effects associated with gaseous explosions on a large scale.

(To be continued).

A SIMPLE SPLASH-PREVENTER FOR LABORATORY TAPS.

By F. W. EDWARDS.

The following simple device has been found very efficient in preventing the splashing of water from laboratory taps. It can be made in a moment, and lasts a fairly long time; it is inexpensive and easily replaceable:—

Procure a piece of *thin* cotton fabric having a fine mesh, and cut out from it two squares of sufficient size. Place these, one above the other, over the mouth of the tap, then slip over them a piece of rubber tubing about an inch in length and of the same bore as the tap. The rubber will hold the fabric in place, but if necessary it may be wired on. Cut off the pieces of fabric that project above the rubber.

It will be found better to employ two, or more, layers of *thin* fabric than one thick one, and large taps usually equire three or four layers.

White Clay of Pfirsching (Germany).—The manufacturing of this mineral, highly effective in fixing basic tar-dye stuffs, and used in most manufactories of colours in Germany and abroad, has been conferred upon Daum and Merkel, Schlegelsmuhle b/Lauterhofen, Obpfiz, Bayern, by the Pfirschinger Mineralwerke G.m.b.H., Kitzingen a/M.

AN ABSOLUTE MANOMETER.*

By MARTIN KNUDSEN.

A gas molecule which impinges against a solid wall is repelled in a direction which is quite independent of the direction of its approach, and a great number of molecules which strike a unit of surface of a solid wall when they are repelled distribute themselves according to the cosine law, provided that there is equilibrium of temperature between the gas and the wall. If there is not equilibrium of temperature between the wall and the molecules the velocities of the molecules are altered by the impact, both in magnitude and direction. The author has endeavoured to discover the laws regulating these changes.

By a series of measurements of the forces between two unequally warmed plates in an exhausted space, the author has discovered the principle of a convenient and very sensitive manometer. Since Crookes's discovery of the radiometer in 1873 many physicists have studied this apparatus, but no actual connection between the value of the forces calculated according to the kinetic theory of gases and the experimental results has been found, probably because the differences of temperature produced in the radiometers by the radiation were not directly measured, and the determinations of the gas pressures in the bulb were often very inaccurate.

The mechanical force with which a gas acts on two plates at different temperatures, when it is between and around them, bears a very simple relation to the gas pressure and the magnitude and temperature of the plates, provided that the distance between the plates is negligible in comparison with the mean wave-length of the gas molecules. Inversely, the pressure can be determined by measuring the mechanical force between the plates if the temperature and magnitude of the plates are known. Based on this principle a manometer can be constructed which is independent of the establishment of an absolute vacuum. The total pressure of the gases and vapours in the space is determined and not the partial pressure as with McLeod's manometer. Such an instrument the author calls an absolute manometer.

Experiments have shown that the force K, with which each square centrimetre of two parallel plates at absolute temperatures, T_1 and T_2, repel one another, and the pressure p of the gases and vapours in the space are connected by the equation—

$$p = \frac{2K}{\sqrt{\frac{T_1}{T_2} - 1}} \quad \ldots\ldots\ldots \quad (1).$$

For small differences of temperature this becomes—

$$p = 4K \frac{T_2}{T_1 - T_2} \quad \ldots\ldots \quad (2).$$

The apparatus consists essentially of vertical metal plates firmly fixed in a stand and heated electrically. A movable metal plate is placed parallel to the plates; it forms the arm of a torsion balance by means of which the force between the plates can be measured. The temperatures of the warmed plates and of the movable plate are determined by means of a mercury thermometer. For pressures greater than some thousandths of a mm. of mercury, the apparatus cannot be used as an absolute manometer, for complicated equations hold good, of which (1) is the limiting equation. If p is put equal to—

$$c\frac{2K}{\sqrt{\frac{T_1}{T_2} - 1}} \quad \ldots\ldots\ldots \quad (3).$$

c increases exponentially with increasing pressure. At equal pressures it is less for hydrogen than for oxygen, nitrogen, and carbon dioxide; it varies with the distance

* Abstracted from *Annalen der Physik*, Series IV., 1910, xxxii.

between the plates, and possibly with the temperatures, but not to a great extent. The experimental proof of Equation (1) is made more difficult because Equation (3) converges more slowly towards Equation (1) as the pressure decreases than was to be expected, and because the pressures are so low that it is difficult to determine them with other manometers. But the sensitiveness can be made so great that any pressure, however small, can be determined with the absolute manometer. The experimental testing was performed as follows:—(1). At the ordinary temperature the readings of the absolute manometer were found to be equal to the sum of the pressure, as measured in McLeod's manometer, and the pressure of saturated mercury vapour. (2). When the pressure of the permanent gases in the apparatus was varied and determined by McLeod's manometer and Mariotte's law, it was found that the absolute manometer registered the corresponding variations. (3). A little mercury was introduced into the glass container of the manometer, and the air was pumped out. When a part of the wall was cooled it was found that the reading of the manometer went down exactly as much as the pressure of the saturated mercury vapour had decreased owing to cooling.

If the molecules must have a mean velocity of Ω_1' to be in temperature equilibrium with the one plate and a mean velocity of Ω_2' to be in equilibrium with the other, then the mean velocities Ω_1 and Ω_2, which the gas molecules actually received when they strike against the plates, must be given by the equation $\Omega_1 + \Omega_2 = \Omega_1' + \Omega_2'$. This equation is satisfied if $\Omega_1 = \Omega_1'$ and $\Omega_2 = \Omega_2'$, but experiments with hydrogen seem to show that this is not the case. If in each cc. of space between the plates A_1 and A_2 (Fig. 1) there are N_1 molecules with mean velocity

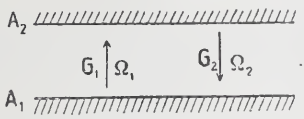

Fig. 1.

Ω_1 from A_1 to A_2, the mean value of the square of their velocities being G_1^2, and if there are N_2 molecules with a velocity in the opposite direction, having the mean velocity Ω_2 and mean square G_2^2, then the gas pressure K′ on the inner sides of the plates is given by—

$$K' = \tfrac{1}{3}m(N_1 G_1^2 + N_2 G_2^2) \quad . \quad . \quad . \quad . \quad (4),$$

where m is the mass of a molecule. Since the energy of the gas molecules is $\frac{1}{2}N_1 m G_1^2 + \frac{1}{2}N_2 m G_2^2$ here, as in a mass of a gas at constant temperature, $K' = \frac{2}{3}E'$. Thus K′ has the same value in all directions, but the pressure between the plates is different from the pressure outside them. The numbers of molecules must be inversely proportional to the mean velocities. Thus,—

$$N_1\Omega_1 = N_2\Omega_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5),$$

i.e., each unit of surface receives the same number of impacts in each second. The number of impacts which each unit of surface of plate A_2 receives is $\frac{1}{4}2N_1\Omega_1$, and plate A_1 $\frac{1}{4}2N_2\Omega_2$. If in unit of time N_1 new molecules are introduced into each cc. of the space between the plates, their velocities being equal and in the opposite direction to the original N_1 molecules, and similarly N_2 molecules in the other direction, then in each cc. of the space there are $2N_1 + 2N_2$ molecules, Each square cm. of the surface will be struck by $\frac{1}{4}2N_1\Omega_1$ molecules of the first kind and $\frac{1}{4}2N_2\Omega_2$ of the second; *i.e.*, by $\frac{1}{2}(N_1\Omega_1 + N_2\Omega_2)$ molecules per second; but this assumes that there are twice as many molecules as there really are, so that the total number is actually $\frac{1}{4}(N_1\Omega_1 + N_2\Omega_2)$.

Thus in the stationary state—

$$\tfrac{1}{4}N\Omega = \tfrac{1}{4}(N_1\Omega_1 + N_2\Omega_2),$$

which gives from (5).

$$N_1\Omega_1 = N_2\Omega_2 = \tfrac{1}{2}N\Omega \quad . \quad . \quad . \quad . \quad . \quad (6).$$

If the warm plate A_1 is fixed and A_2 is movable and has the same temperature as the surrounding gas, its pressure p is given by $p = \frac{1}{3}NmG^2$. On the inner side of the plate A_2 the pressure is K′ and on the outer p. Therefore K, the resultant force per unit of surface, is given by—

$$K = K' - p = p\left(\frac{K'}{p} - 1\right).$$

From (4),—

$$K = p\left[\frac{N_1 G_1^2 + N_2 G_2^2}{NG_2} - 1\right],$$

which gives, from (6),—

$$K = p\left(\frac{1}{2}\,\frac{\frac{G_1^2}{\Omega_1} + \frac{G_2^2}{\Omega_2}}{\frac{G^2}{\Omega}} - 1\right).$$

From Maxwell's Law of Distribution of Molecular Velocities—

$$\frac{G}{\Omega} = \sqrt{\frac{3\pi}{8}}.$$

For small differences of temperature—

$$\frac{G}{\Omega} = \frac{G_1}{\Omega_1} = \frac{G_2}{\Omega_2};$$

Therefore—

$$K = p\left(\frac{1}{2}\,\frac{G_1 + G_2}{G} - 1\right) = p\left(\frac{1}{2}\,\frac{\Omega_1 + \Omega_2}{\Omega} - 1\right). \quad (7).$$

If we assume that the velocity with which a molecule leaves a solid wall is dependent on the temperature and on the velocity of approach, then the relation must be such that as G_1, which is a function of G_1' and G_2, converges towards G_1', G_2 does the same. This condition is satisfied if—

$$G_1 \quad G_2 + \alpha(G_1' - G_2).$$

Similarly—

$$G_2 = G_1 + \alpha(G_2' \quad G_1),$$

or by adding—

$$G_1 + G_2 = G_1' + G_2',$$

for all values of G_1 and G_2. But the gas which surrounds the plates is in equilibrium with the plate A_2 and thus $G = G_2'$. Putting $G_1' + G_2'$ for $G_1 + G_2$ (7) becomes—

$$K = \frac{p}{2}\left(\frac{G_1'}{G_2'} - 1\right) = \frac{p}{2}\left(\frac{\Omega_1'}{\Omega_2'} - 1\right).$$

But—

$$\frac{G_1'}{G_2'} = \frac{\Omega_1'}{\Omega_2'} = \sqrt{\frac{T_1}{T_2}};$$

where T_1 and T_2 are the absolute temperatures of the two plates. Therefore—

$$K = \frac{p}{2}\left(\sqrt{\frac{T_1}{T_2}} \quad 1\right) \text{ or } p = \frac{2K}{\sqrt{\frac{T_1}{T_2}} - 1} \text{ dynes per sq. cm.} \quad (8).$$

For small differences of temperature this equation becomes—

$$K = \frac{p}{4}\,\frac{T_1 - T_2}{T_2} \text{ or } p = 4K\,\frac{T_2}{T_1 - T_2} \text{ dynes per sq. cm.} \quad (9).$$

In the first apparatus the warm plate A_1 (Fig. 2) consisted of a vertical strip of platinum foil of height about 10 cm., breadth 1 cm., thickness 0·00025 cm. The plate A_2 also consisted of platinum, its dimensions being

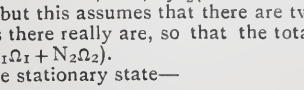

Fig. 2.

10 × 4·3 × 0·01 cc. It was provided with a small mirror, and was suspended by a platinum wire 2·5 cm. long and 0·1 mm. thick, marked O in the figure. The moment of

inertia was 15·03 grms. per cc., and the time of oscillation 1·902 seconds (complete oscillation). The distance of the middle of A_1 from the axis of oscillation was 1·145 cm. When the air in the apparatus was exhausted to a pressure of 4 cm. of mercury, warming produced no repulsion. When the air was further rarefied a repulsion was obtained which increased as the temperature was raised, and for a given difference of temperature increased as the pressure decreased, till the repulsion reached a maximum, and then began to decrease. The mean value of the pressure in a series of experiments, in which the difference of temperature varied from 8° to about 346° and the pressure was low, was found to be 2·28 dynes per square cm. With McLeod's manometer the corresponding value was 2·24 dynes per square cm. At higher pressures the agreement

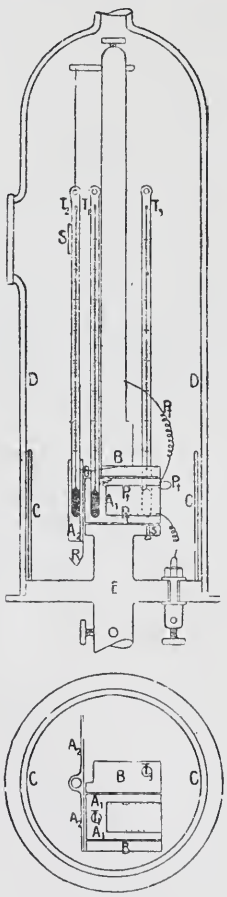

FIG. 3.

of the two readings was not satisfactory. Thus it appears that the absolute manometer when constructed in this way can only be employed for very low pressures.

A more rational form of the manometer is shown in Fig. 3. A copper block B B was fixed on the metal plate E of the air-pump D. A copper cylinder, A_1, was introduced into a cylindrical hole in this block; it was held in position by six glass points, and its polished end was placed as close as possible to one surface of the copper block. The cylindrical space between the cylinder and block was 0·0174 cm. The diameter of the cylinder was 1·63 cm. It was warmed by a platinum wire, and the temperature was measured by a mercury thermometer, T_1, which passed through a hole in the cylinder, and was connected with the cylinder by means of tin-foil or a fusible alloy. The metal plate, A_2, was suspended parallel to the polished end of the cylinder; the thermometer, T_2, was inserted through this plate, and was furnished with the reading mirror, S. The suspension wire (½ mm.) was fastened to the thermometer and to the copper plate. C C represents a blackened metallic tube by which the temperature of the copper block, the plate of the pump, and the copper plate, which is also blackened, could be equalised. Two little windows in C C enabled the width of the space between the copper plate and cylinder or block to be measured. The distance of the axis of the cylinder from the axis of suspension of the copper plate was 1·233 cm The effective area of the warm plate was 2·133 sq. cm. The moment of inertia was 19·05, and the time of one complete oscillation was 2·46 seconds. The distance between the warm plate and the movable plate was 0·012 cm. With this form of apparatus using hydrogen it was found that there was a very good agreement between the numbers obtained at different differences of temperature, but the actual pressure was 1·33 times as great as that calculated from the repelling force.

It was found that at low pressures the calculated pressure p is equal to p', the pressure registered by McLeod's gauge. As the pressure increases p differs more and more from p', being always less than p'. From the results it looks as if p'/p converges to 1 as the pressure approaches 0, but this conclusion requires confirmation, using a new apparatus.

A small apparatus was constructed and connected with a McLeod's manometer to determine the pressure of mercury vapour, for which purpose it was found to be very satisfactory. By these experiments it was found that (9) is only an approximate formula, (8) agreeing better with the results obtained.

In the form of apparatus which is the easiest to construct and is also in many respects the most convenient, the case consists of a vertical glass tube, A (Fig. 4), of

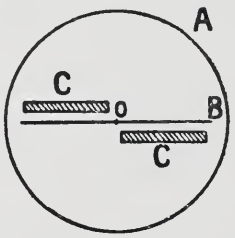

FIG. 4.

diameter about 2·5 cm. C C are two strips of glass about 0·2 cm. thick and 1 cm. broad, and are connected with one another, top and bottom, by means of pieces of iron. The suspension thread, O, is fastened to the upper connecting piece. The movable plate, B, is made of mica, and is 2 cm. broad and 4 cm. long. Connected with this plate is a small horizontal iron wire 1 cm. long and 0·15 cm. thick; this enables a magnet to be used to give the mica leaf a definite position of equilibrium. If the part of the tube A surrounding the mica leaf is warmed, the latter is strongly impelled towards the places where it is not protected by the strips C, and hence it is deflected away from these strips. If the external magnets are arranged so that a time of oscillation (complete oscillation) of 1·848 seconds is obtained, the sensitiveness is such that for a difference of temperature of 37° and a scale distance of 0·485 m. a pressure of 0·485 dynes per sq. cm. is obtained, giving a displacement of 226 mm. Hence each mm. displacement corresponds to a pressure of about 0·002 dynes per sq. cm. The pressure is determined by the deflection, which is caused by a given alteration of temperature of the tube A, but depends to a certain extent upon the temperature of the rods and mica plate, so that a thermometer is introduced into the interior of the apparatus, or care must be

taken that the warming of the tube, A, does not last so long that the rods and plate are appreciably warmed. Hence the rods must not be connected with the tube at places where the latter is warmed, and, moreover, it is best to use for the apparatus only such materials as are not affected by mercury. Possibly at very low pressures a correction should be made for the pressure of light. This can very easily be determined if the warming is performed electrically, when the emitted energy can be ascertained with sufficient accuracy.

SPECIFIC GRAVITIES AT THE MELTING-POINT IN RELATION TO CONSTITUTION.

By J. C. EARL.

Assume that the carbon, hydrogen, and oxygen atoms are spheres of equal size, when in combination, at the melting-point of the substance in which they are combined. This is a natural conclusion of the shape of the atoms at the point when the substance containing them changes from a rigid solid structure to a mobile liquid.

Consider the case of water at 0° C. The molecule H_2O at this temperature will consist of three perfect spheres of equal size, just touching one another. There will therefore be interstices between these spheres and also between the spheres constituting this molecule and those constituting surrounding molecules. Therefore the actual volume taken up by the molecule will be $3 \times \frac{4}{3}\pi r^3$ plus the volume of the interstices within and surrounding it. In the case of water the number of these interstices is 8 $(= 2 \times 3 + 2)$.

Therefore the volume of the water molecule at 0° C. $= 3 \times \frac{4}{3}\pi r^3 + 8x$; where x is the volume of one interstice. x can be solved by considering the case of palmitic acid, for example, whose specific gravity at the melting-point is accurately known. The value of r can be taken as unity as it is constant for carbon, hydrogen, and oxygen, whatever compound of these elements is taken.

Volume of palmitic acid molecule $= 50 \times \frac{4}{3}\pi r^3 + 102x$.

$$\text{Sp. gr.} = 0{\cdot}853 \text{ at m. p.} = \frac{\text{weight of the molecule}}{\text{volume of the molecule}}.$$

$$\therefore\ 0{\cdot}853 = \frac{256{\cdot}3 \text{ (mol. wt. of palmitic acid)}}{50 \times \frac{4}{3}\pi r^3 + 102x}$$

$$\therefore\ x = 0{\cdot}894.$$

From this general formula—

$$\text{Sp. gr.} = \frac{\text{M.W.}}{n \times \frac{4}{3}\pi + (2n+2)\,0{\cdot}894}$$

(n = number of atoms in molecule at melting-point)

the specific gravity of any compound of carbon, hydrogen, and oxygen can be calculated at its melting-point.

Some results which fairly support the formula are appended :—

	Actual.	Calculated from formula.
Lauric acid ..	0·875	0·874
Myristic acid ..	0·862	0·862
Stearic acid ..	0·845	0·845
Water	0·916	0·913
Cetyl alcohol ..	0·8172	0·79
Docosane	0·7782	0·764

There are many cases in which the formula does not hold good, but surely the above results cannot be mere coincidence. In the case of organic compounds containing elements other than carbon, hydrogen, and oxygen, the difference between the calculated specific gravity and that given in the tables is very great.

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PROCEEDINGS OF SOCIETIES.

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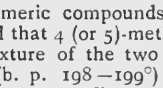
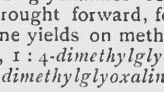
(Concluded from p. 257).

235. "*The Tautomerism of Glyoxalines and the Constitution of Pilocarpine.*" By Frank Lee Pyman. (*Trans.*, 1910, 1814).

Otto Fischer (*Journ. Prakt. Chem.*, 1906, [2], lxxiii., 419; 1907, [2], lxxv., 88) has already shown that benziminazoles are tautomeric, and Jänecke (*Ber.*, 1899, xxxii., 1098) and Gabriel (*Ber.*, 1908, lxi., 1926) have made it seem probable that simple glyoxalines behave similarly. Conclusive evidence that simple glyoxalines react as tautomeric compounds is now brought forward, for it is found that 4 (or 5)-methylglyoxaline yields on methylation a mixture of the two isomerides, 1 : 4-*dimethylglyoxaline* (I.) (b. p. 198—199°) and 1 : 5-*dimethylglyoxaline* (II.) (b. p. 224—225°) :—



I.



II.

Jowett and Potter (*Trans.*, 1903, lxxxiii., 464) by the methylation of 4(or 5)-methylglyoxaline obtained a dimethylglyoxaline which they regarded as a simple substance, but which was not identical with the dimethylglyoxaline obtained by Jowett (*Trans.*, 1903, lxxxiii., 438) from *iso*pilocarpine. It is now shown that the latter compound is identical with 1 : 5-dimethylglyoxaline, and that Jowett and Potter's dimethylglyoxaline was a mixture of the 1 : 4- and 1 : 5-isomerides, consisting mainly of the former.

The methylation of *bromo*-4(or 5)-*methylglyoxaline* and *dibromo*-4(or 5)-*methylglyoxaline* yields in each case a mixture of two isomeric N-*methyl* derivatives which have been separated and characterised. The bromination of 1 : 4- and 1 : 5-dimethylglyoxaline leads to the formation of one of the bromodimethylglyoxalines and one of the dibromodimethylglyoxalines in each case.

236. "*Kinetics of the Reaction between Silver Salts and Aliphatic Iodides.*" By Frederick George Donnan and Harold Edward Potts. (*Trans.*, 1910, 1882).

The experiments of Burke and Donnan (*Trans.*, 1904, lxxxv., 555) have shown that the reaction between silver nitrate and an alkyl iodide in alcoholic solution is disturbed by an accelerating effect due to one of the products. In the present paper it is shown that in the reaction between silver lactate and ethyl iodide in aqueous alcohol, the accelerating effect disappears. It is also shown that in the reaction between silver nitrate and ethyl iodide in a non-hydroxylic solvent (acetonitrile) when no free (nitric) acid is produced, the kinetic behaviour does not essentially differ from that observed in alcoholic and aqueous solutions. The reaction between iodoform and silver nitrate in alcoholic solution follows the same pseudo-bimolecular equation as the reaction between a mono-iodide and silver nitrate. It was found that methylene iodide reacts very sluggishly with silver nitrate in alcoholic solution. Owing to the rapid decomposition of carbon tetraiodide in alcoholic solution, comparative experiments with this substance could not be carried out with sufficient accuracy. Although the matter could not be decisively settled, the general trend of the experimental evidence is in favour of the view that it is the undissociated silver salt which reacts with the alkyl iodide in the first instance, with the formation, possibly, of a transient intermediate product. The suggestion is made that the constancy of the velocity-coefficient in any particular reaction is due to a compensation of the decrease due to the increasing relative ionisation of the silver salt by the acceleration referred to above. Senter's suggestion that the acceleration is due to the silver halide produced is discussed.

237. "*The Identity of Osyritrin, Myrticolorin, Violaquercitrin, and Rutin.*" By Arthur George Perkin. (*Trans.*, 1910, 1776).

It has been shown (*Trans.*, 1902, lxxxi., 477) that osyritrin, myrticolorin, and violaquercitrin are identical. Schmidt (*Arch. Pharm.*, 1908, ccxlvi., 214) and Wunderlich (*Ibid.*, ccxlvi., 224) have found that when hydrolysed violaquercitrin gives, in addition to quercetin and dextrose, also rhamnose, and that this glucoside is identical with rutin, which yields the same products. It therefore appeared certain that osyritin and myrticolorin in reality consist of rutin, and this has been found to be the case.

238. "*A Glucoside from* Tephrosia purpurea." By George Clarke, jun., and Shrish Chandra Banerjee. (*Trans.*, 1910, 1833).

Tephrosia purpurea (Pers.), nat. ord. *leguminosæ*, contains a yellow crystalline glucoside (Clarke and Banerjee, *Proc.*, 1909, xxv., 16). This substance has been further investigated, and has the formula $C_{27}H_{30}O_{16},3H_2O$. When hydrolysed, it is decomposed into quercetin, dextrose, and rhamnose according to the equation $C_{27}H_{30}O_{16}+3H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6 + C_6H_{12}O_5,H_2O$.

It is identical with rutin described by Schunk (*Trans.*, 1888, liii., 264), which therefore has the above formula, and not that hitherto ascribed to it.

239. "*The Molecular Complexity of Amides in various Solvents.* Part III. *Amides in Aqueous Solution.*" By Andrew Norman Meldrum and William Ernest Stephen Turner. (*Trans.*, 1910, 1805).

In continuation of their previous work (*Trans.*, 1908, xciii., 876); 1910, xcvii., 1605) the authors have determined the molecular complexity of fourteen additional amides in aqueous solution. Water, by reason of its high dielectric constant, should prevent association of the solute, according to the Nernst-Thomson rule. The authors find that fifteen out of the total of twenty-three amides examined are associated in water.

The authors hold that association in water is of frequent occurrence, and has been ignored in the study of aqueous solutions to an injurious extent. They find that during the hydrolysis of ethyl acetate, or the inversion of sucrose, by hydrochloric acid, the presence of methylacetanilide, an associated substance, has an effect similar to that caused by the presence of sodium chloride, as observed by Caldwell (*Proc. Roy. Soc.*, 1906, A, lxxviii., 272) and H. E. Armstrong (*loc. cit.*, 1907, A, lxxix., 576). The accelerations due to equal weights of the two foreign substances are approximately the same.

240. "*Optically Active Salts of* 4-*Oximino*cyclo*hexanecarboxylic Acid and the Configuration of the Oximino-Group.*" By William Hobson Mills and Alice Mary Bain. (*Trans.*, 1910, 1866).

If morphine (1 mol.) is added to the ethyl-alcoholic solution of 4-oximino*cyclo*hexanecarboxylic acid, the morphine salt which separates contains a dextrotatory form of the acid, for on decomposing it with excess of ammonia and removing the morphine, the solution of ammonium salt obtained is strongly dextrorotatory, the molecular rotation varying from $[M]_D$ 50° to $[M]_D$ 60° in different preparations. Similarly, from the quinine salt (*Proc.*, 1909, xxv., 178), which has been crystallised from water, the corresponding lævorotatory ammonium salt, $[M]_D$ −70° to −80°, has been obtained. That the substances to which these optically active solutions of ammonium salt owe their rotatory power are the normal ammonium salts of dextro- and lævo-rotatory forms of 4-oximino*cyclo*hexanecarboxylic acid was shown by treating the solutions with silver nitrate. The substances thus precipitated were pure silver salts of this acid, and when treated with an aqueous solution of sodium chloride they gave respectively dextro- and lævo-rotatory solutions of the corresponding sodium salts, the molecular rotations observed being $[M]_D$ 74·5° and −79·9°. Autoracemisation takes place very rapidly in neutral solutions of these optically active salts, but it is greatly retarded by the presence of excess of alkali.

By these experiments the existence of a new type of optically active substances is demonstrated, the molecular asymmetry of which is determined by the peculiar configuration of the doubly linked tervalent nitrogen atom. In addition, direct proof is afforded that in the oximino-group the three valencies of the nitrogen atom are directed along the three edges of a trihedral angle, as was postulated by Hantzsch and Werner (*Ber.*, 1890, xxiii., 11).

241. "*The Resolution of Benzoyloscine.*" By Frank Tutin. (*Trans.*, 1910, 1793).

Benzoyloscine (benzoylscopoline) has been resolved by the fractional crystallisation of its d-*bromocamphorsulphonate*. *Benzoyl*-d-*oscine* d-*bromocamphorsulphonate* forms needles, which melt at 246°, but *benzoyl*-l-*oscine* d-*bromocamphorsulphonate* could not be obtained in a state of purity. *Benzoyl*-d-*oscine hydrochloride* melts at 283—284°; the corresponding *nitrate* at 200°; the *picrate* at 211—212°; and the *aurichloride* at 189—190°.

Benzoyl-d-*oscine* has $[\alpha]_D$ +3·5° in 50 per cent alcohol, whilst the ion of this base has $[\alpha]_D$ +10·0°, calculated from the rotation of its *d*-bromocamphorsulphonate.

d-*Oscine* was prepared in the form of its *hydrochloride* by hydrolysing benzoyl-*d*-oscine with hydrochloric acid. It has a specific rotation of about +77·7°.

Benzoyloscine d-*camphorsulphonate* melts at 167—168°, and forms microscopic diamond-shaped crystals, but it could not be resolved by fractional crystallisation.

242. "*Carboxylic Acids of* cyclo*hexanone and some of its Derivatives.*" By Henry Dent Gardner, William Henry Perkin, jun., and Hubert Watson. (*Trans.*, 1910, 1756).

A detailed account of an investigation of which a preliminary note has already appeared (*Proc. Chem. Soc.*, xxvi., 136).

243. "*Note on the Constitution of α-Elaterin.*" By Charles Watson Moore. (*Trans.*, 1910, 1797).

The following formulæ have, at various times, been suggested for elaterin:—$C_{20}H_{28}O_5$ (Zwenger); $C_{22}H_{30}O_6$ (Thoms); $C_{24}H_{34}O_6$ (Hemmelmayr); and $C_{28}H_{38}O_7$ (Berg). The present author has now obtained results which prove the correctness of the empirical formula suggested by Berg. The presence of an acetyl group in elaterin has been confirmed, but it has been shown that this substance contains no ketonic or aldehydic group. Two crystalline substances have been obtained by the oxidation of "elateric acid," which have been shown to possess the formulæ $C_{24}H_{32}O_4$ and $C_{24}H_{30}O_5$ respectively. The latter of these is a diketone, and has been designated *elaterone*. On distillation with zinc dust, elaterin yields 1 : 4-dimethylnaphthalene.

The results so far obtained indicate that the formula of elaterin may be represented as follows:—

$$C_{25}H_{33}O\begin{cases}-OH\\-OH\\-O\cdot CO\cdot CH_3\\-CO\\|\\-O\end{cases}$$

244. "*The Viscosity of Salt Solutions.*" By Malcolm Percival Appleby. (*Trans.*, 1910, 2000).

By the use of specially standardised viscometers of a modified Ostwald type, the viscosities of aqueous solutions of lithium nitrate have been determined at 25°, 18°, and 0° over wide ranges of concentration with an error of not more than 0·01 per cent for solutions less concentrated than normal.

The formula of Grüneisen (*Wiss. Abh. Phys. Tech. Reichs.*, 1905, iv., 151) is found not to represent the phenomena of dilute solution. A method of calculating the viscosity of salt solutions from their hydration numbers, or *vice versa*, has been described. The application of this method to the viscosities of solutions of lithium nitrate at 18° and 25° gives results consistent with the estimates of

ionic hydration made by other observers. The application of the method to some other salts is discussed.

245. "*Some Reactions of Keten. Combination with Hydrocyanic Acid.*" By Stella Deakin and Norman Thomas Mortimer Wilsmore. (*Trans.*, 1910, 1968).

The compound which was mentioned (*Proc.*, 1908, xxiv., 77) as being formed by the action of keten on hydrocyanic acid has been further investigated. In a pure state it is a colourless liquid, which boils undecomposed at 110·2°(corr.)/100 mm., and with slight decomposition at 173°/772 mm. It may be frozen to a white solid, which melts at −196° to −195°. Analysis and determination of molecular weight show that it has the composition $C_5H_5O_2N$. The new substance is decomposed by water with formation of acetic and hydrocyanic acids, and by alcohol in the presence of mineral acids, ethyl acetate and hydrocyanic acid being obtained. It also reacts with aniline, giving acetanilide and hydrocyanic acid. It is tentatively suggested that the new compound may be *α-acetoxyacrylonitrile*, $CH_2{:}C(CN){\cdot}O{\cdot}CO{\cdot}CH_3$, a constitution which is shown to be consistent with the molecular volume, refractivity, and dispersion of the substance.

The actions of magnesium methyl iodide and of nitrosyl chloride on keten have also been studied. With the former acetone is produced, and with the latter chloroacetyl chloride; but in both cases the greater part of the keten condenses with the formation of brown resins.

246. "*The Polymerisation of Keten.* cyclo*Butan*-1 : 3-*dione* '*Acetylketen*')." By Frances Chick and Norman Thomas Mortimer Wilsmore. (*Trans.*, 1910, 1978).

The research on the polymerisation of keten (*Trans.*, 1908, xciii., 946) has been continued, and the first or bimolecular polymeride has been more fully studied. This substance combines with bromine to form a bromoacetoacetyl bromide, which with alcohol gives γ-bromoacetoacetic ester and not the α-derivative, showing conclusively that the bimolecular polymeride is *cyclo*butan-1 : 3-dione and not acetylketen, as previously supposed. From the bromoacetoacetyl bromide an anilide was also obtained, identical with the bromoacetoacetanilide described by Knorr (*Annalen*, 1886, ccxxxvi., 79), which shows that the bromine in this substance is in the γ- and not in the α-position, as believed by him. As a further consequence, the bromohydroxymethylquinoline, obtained by Knorr by the action of sulphuric acid on bromoacetoacetanilide, would seem to have the bromine attached to the methyl group and not to the nucleus, or else the bromine atom must wander from the methyl to the CH_2 group during the condensation. With ammonia, *cyclo*butan-1 : 3-dione forms, in the first place, the acetoacetamide described by Claisen and Meyer (*Ber.*, 1902, xxxv., 583); but by the further action of ammonia an oil is obtained, which appears to consist chiefly of aminocrotonamide, since on heating it gives a compound having the composition $C_8H_{13}O_2N_3$, which is in all probability a lutidine derivative, namely, *4-amino-2 : 4-dimethyl-Δ²-tetrahydro-6-pyridone-3-carboxylamide*. With semicarbazide, *cyclo*butan-1 : 3-dione forms the semicarbazone-semicarbazide of acetoacetic acid. With magnesium methyl iodide, diacetone alcohol appears to be formed in small quantity. With hydrogen in presence of platinum black, *cyclo*butan-1 : 3-dione is reduced to butyraldehyde. It does not react with sodium, with phenylcarbimide, or with hydrocyanic acid. On long keeping, or on warming, it polymerises with formation of dehydracetic acid.

Much work has been done with a view to elucidating the nature of the yellow crystalline compound, which is formed from *cyclo*butan-1 : 3-dione in the presence of quinoline; but so far no clue to its constitution has been found. Its empirical formula is, however, $C_{13}H_{10}O_3$. It is possibly a naphthalene derivative.

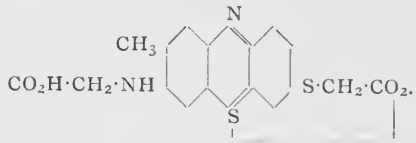
247. "*Aromatic Antimony Compounds.* Part I. *The Oxidation and Nitration of Triphenylstibine.*" By Percy May (*Trans.*, 1910, 1956).

A description is given of the nitration of triphenylstibine, a preliminary account of which has already appeared (*Proc. Chem. Soc.*, xxvi., 142). The behaviour of triphenylstibine towards various oxidising agents, such as concentrated sulphuric acid, and potassium permanganate, is described, and the relation between various derivatives of triphenylstibine oxide, and the influence of the nitro-group in the molecule are also discussed.

248. "*Contributions to our Knowledge of the Sulphide Dye-stuffs.*" Part I. By George Herbert Frank.

It has been found that many colouring matters belonging to the "sulphide" class readily combine with chloroacetic acid, giving carboxylic derivatives which are readily soluble in alkalis.

The colouring matter known as immedial-indone gives a dicarboxylic derivative, $C_{17}H_{14}O_4N_2S_2$ (Found, M.W. = 377), which requires, for its reduction to the leuco-compound, two atoms of hydrogen per molecule. The suggested constitution for this dicarboxylic derivative is—



249. "*The Constituents of Leptandra.*" By Frederick Belding Power and Harold Rogerson. (*Trans.*, 1910, 1944).

The material employed for this investigation was commercial "leptandra," consisting of the dried rhizome and roots of *Veronica virginica*, Linné (*Leptandra virginica*, Nuttall).

A concentrated alcoholic extract of this material, when distilled in a current of steam, yielded a small amount of an essential oil. The latter was a dark coloured liquid, which distilled between 120° and 160°/25 mm.

The portion of the extract which was soluble in water contained 3 : 4-dimethoxycinnamic acid, $C_6H_3(OMe)_2{\cdot}CH{:}CH{\cdot}CO_2H$ (m. p. 180–181°); a quantity of mannitol, amounting to 2·14 per cent of the weight of the drug; and a sugar which yielded *d*-phenylglucosazone (m. p. 209—211°), together with tannic and colouring matter. It yielded, furthermore, a quantity of an amorphous product, which possessed an intensely bitter, nauseous taste, and amounted to 1·6 per cent of the weight of the drug. By the hydrolysis of this product there were obtained, besides resinous material, cinnamic and *p*-methoxycinnamic acids.

The portion of the extract which was insoluble in water consisted chiefly of a dark brown resin, which amounted to 6·2 per cent of the weight of the drug. From this resin the following substances were obtained:—A phytosterol, $C_{27}H_{46}O$ (m. p. 135—136°); $[\alpha]_D$ −33·0°), the acetate of which melts at 119—120°, and which it is proposed to designate *verosterol*; a mixture of fatty acids, consisting apparently of oleic, linolic, palmitic, and stearic acids; *p*-methoxycinnamic acid, $OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$ (m. p. 170°), which was present in the form of an ester, and a very small amount of 3 : 4-dimethoxycinnamic acid.

It has not been possible to confirm the statement recorded in the literature that "leptandra" contains a crystalline bitter glucoside, designated as "leptandrin," to which its activity may be attributed, nor does it contain a saponin, as has been asserted.

250. "*The Formation of Tolane Derivatives from p-Chlorotoluene and 3 : 4-Dichlorotoluene.*" By James Kenner and Ernest Witham. (*Trans.*, 1910, 1960).

The anomalous formation of a tolane derivative during the preparation of benzotrichloride from toluene, described by Liebermann and Homeyer (*Ber.*, 1879, xii., 1971), was also observed by Armstrong and Wynne during the conversion of *p*-chlorotoluene and of 3 : 4-dichlorotoluene into the corresponding chlorobenzylidene dichlorides. The present authors have investigated these toluene derivatives

with the view of determining the conditions leading to their formation.

To aid in the study of this condensation, 4 : 4′-dichlorotolane tetrachloride has been obtained by the action of copper powder on *p*-chlorobenzotrichloride. The method gives only moderate yields, and, as previously found by Fox (*Ber.*, 1893, xxvi., 653), and now confirmed by the authors, breaks down when applied to the case of *o*-chlorobenzotrichloride.

cis- and *trans*-4 : 4′-Dichlorotolane dichlorides, melting at 166—167° and 86—87° respectively, result from the action of zinc dust on the tetrachloride in alcoholic solution at 50° for two days, although under these conditions some of the *cis*-isomeride is further reduced to 4 : 4′-dichlorotolane (m. p. 175—176°), whilst at the boiling-point the conversion is complete. Both the *cis*-2 : 2′- and 4 : 4′-dichlorotolane dichlorides under similar conditions give the corresponding dichlorotolanes.

251. "*The Effect of Temperature on the Equilibrium* $2CO \rightleftarrows CO_2 + C$." By THOMAS FRED ERIC RHEAD and RICHARD VERNON WHEELER.

The equilibrium between carbon monoxide, carbon dioxide, and carbon has been determined for every 50° between 850° and 1100° and for 1200°.

The method adopted has been to circulate carbon dioxide continuously over purified wood charcoal heated in an electric resistance furnace of special construction until the pressure in the apparatus attained a constant value.

The values obtained for the equilibrium are as follow:—

	Per cent by volume.	
Temperature.	Carbon dioxide.	Carbon monoxide.
850°	6·23	93·77
900	2·22	97·78
950	1·32	98·68
1000	0·59	99·41
1050	0·37	99·63
1100	0·15	99·85
1200	0·06	99·94

From the equation—

$$\frac{19{,}500}{T} + \log_e \frac{c_1^2}{c_2} = k$$

(derived from Le Chatelier's general equation for equilibrium in gaseous systems), the following values for k are obtained:—

T.	k.
1123	20·01
1173	20·39
1223	20·24
1273	20·44
1323	20·32
1373	20·70
1473	20·65

252. "*The Molecular Complexity in the Liquid State of Tervalent Nitrogen Compounds.*" By WILLIAM ERNEST STEPHEN TURNER and ERNEST WYNDHAM MERRY.

The molecular complexities of nearly forty organic nitrogen compounds, comprising amines, nitrosoamines, nitriles, and amides have been determined by Ramsay and Shields' method; one, and the main, object of the investigation being to ascertain if the molecular association in the amides can be ascribed to the action of the unsaturated valencies of the nitrogen or oxygen atom present in the amido-group.

Primary amines were found to be slightly associated. Secondary and tertiary amines gave abnormally high values of the Ramsay and Shields' constant, and the results raised the question of the validity of the Ramsay and Shields' formula.

The aliphatic nitrosoamines and aliphatic nitriles are associated; the aromatic members of these two groups of compounds are either only slightly or non-associated.

The amides and anilides examined are associated, the extent of association being of the same order as found in the aliphatic alcohols and acids. The aromatic amides, benzamide, and salicylamide are strongly associated. Below 80°, formamide is more highly associated than water, but the molecular complexity decreases rapidly with rise of temperature.

It was concluded that the cause of molecular association in the amides cannot be directly ascribed to the unsaturated character of the nitrogen or oxygen atom, and that association only occurs when these elements are found in combination in electronegative groups.

ROYAL SOCIETY.

Ordinary Meeting, November 10th, 1910.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Tidal Observations of the British Antarctic Expedition, 1907.*' By Sir GEORGE DARWIN, K.C.B., F.R.S.

"*A Mistake in the Instructions for a certain Apparatus in Tidal Reductions.*" By Sir GEORGE DARWIN, K.C.B., F.R.S.

"*Conduction of Heat through Rarefied Gases*" (II.). By FREDERICK SODDY, M.A., F.R.S., and ARTHUR JOHN BERRY, B.A.

The thermal conductivities of argon, helium, and hydrogen at very low pressure have been examined in greater detail with new and improved apparatus. The hypothesis provisionally put forward (*Proc. Roy. Soc.*, 1910, A, lxxxiii., 254) that the interchange of energy on impact is imperfect in the lighter gases, has been tested and found not to account for the smallness of the ratio (K/Q) of the found to the calculated conductivities. The conductivity of hydrogen using a palladium hot wire is the same as that with a platinum wire. Change of temperature of the hot surface, that of the cold surface remaining constant at room temperature, does not exert so much influence on the value of K as was anticipated.

The value of K/Q tended to diminish as the difference of temperature increased, especially at high temperatures. At low temperatures, attained by immersing the apparatus in liquid air and in solid carbon dioxide and ether, the ratio K/Q is *diminished*, whereas on the hypothesis of imperfect interchange of energy an increase was expected. Jacketing the apparatus with vapours up to 264° caused an increase in the value of K/Q. It appears that, most probably, increase in the difference of temperature between the surfaces tends to decrease the value of K/Q, whereas increase in the temperature of both surfaces increases it.

Argon under some of the new conditions tried conforms to the theory hardly better than the other gases, and the agreement found previously was probably fortuitous. The general conclusion is that the conductivity at low pressures varies less with the nature of the gas and with the temperature of the experiment than is to be expected from kinetic considerations. The extreme values found for the conductivities of the three gases over a range of about 450° lay between 0·8 and 3·4, whereas the calculated values lie between 0·95 and 16·2 (X 10^{-5} calorie, per sq. cm. of hot surface, per 1° difference of temperature, per 0·01 mm. pressure of gas).

"*Chemical Physics involved in the Precipitation of Free Carbon from the Alloys of the Iron-Carbon System.*" By W. H. HATFIELD, B.Met.

The intention of the author is to examine the conditions under which free carbon is produced in iron and steel. Whereas it has been an open question as to whether or not free carbon could be produced direct from the solid solution, the paper is intended to prove the truth of the theory that free carbon can only be produced by the dissociation of the free carbide. It is hoped to demonstrate that this theory holds good through the whole range of the alloys in which free carbon, whether as graphite or annealing carbon, is found.

After the presentation of evidence in support of this view of the production of graphite in and near the freezing range, experiments, performed to determine the chemical physics underlying the liberation of annealing carbon in white cast-iron, are described. By the electrolytic method of analysis the cementite carbide was obtained from such irons of varying composition, and it is shown how, by varying the percentage of silicon, manganese, or sulphur in the iron, the composition of the cementite is modified and its degree of stability at varying temperatures determined. It is also shown that the size and structure of the precipitated annealing carbon is largely due to the size and structure of the original cementite.

Experiments performed to produce annealing carbon in blister steel during the cementation process are then described; after which an explanation of the phenomena of "black" steel is discussed; it is shown that the free carbon found in such steels may present one of two formations, each produced under different conditions. The author further endeavours to demonstrate that whilst the free cementite carbide is dissociated at high temperatures through the whole range of the alloys, the carbide remaining in solid solution does not dissociate until the resolution of the solid solution into the carbide and iron of the pearlite, at the carbon change point.

"*Spectroscopic Investigation of the Nature of the Carriers of Positive Electricity from Heated Aluminium Phosphate.*" By F. Horton, M.A., D.Sc.

The emission of positive ions from substances heated in a vacuum has been investigated by several experimenters, and it has been found that the ratio of the charge to the mass of the ions is the same for all the substances so far experimented on. Assuming that the charge is equal to that carried by the hydrogen ion in electrolysis, the mass of the carriers of positive electricity from heated substances must be about twenty-six times that of the hydrogen atom. The object of this research was to obtain the spectrum of these ions.

Aluminium phosphate was chosen for investigation because of the very large positive ionisation produced on heating this substance. A calculation showed that, with the apparatus used, it might be expected to collect a sufficient quantity of the carriers to obtain their spectrum in a small vacuum tube. The vessel used to collect the carriers was cooled in liquid air during the passage of the thermionic current from a strip of platinum covered with aluminium phosphate to a surrounding platinum cylinder. The material collected was then allowed to vaporise and its spectrum was obtained by rendering it luminous with an electrodeless ring discharge. The spectrum of carbon monoxide was always obtained, although precautions had been taken to exclude this gas, or materials which might give rise to it, from the apparatus. It is concluded, therefore, that the positive ions consist of carbon monoxide, the molecular weight of which agrees fairly well with that required by the results of the e/m determinations.

It is considered improbable that this gas is evolved on heating every substance which has been experimented on in the determinations of the specific charge, but from the nature of the apparatus used, it must always have been present during these determinations. In the paper, reasons are given for believing that molecules of carbon monoxide readily act as carriers of positive electricity, and this gas probably diffuses into the hot metal or other substance and is evolved in an ionised state.

"*Determination of the Tension of a Recently-formed Water-surface.*" By N. Bohr.

Arguments in further support of the author's previous conclusion, that the surface tension does not change sensibly with the time that has elapsed since the surface was formed.

"*Aerial Plane Waves of Finite Amplitude.*" By Lord Rayleigh, O.M., F.R.S.

"*Anomalous Behaviour of Delicate Balances, and an Account of Devices for Increasing Accuracy in Weighings.*" By J. J. Manley.

"*Improbability of a Random Distribution of the Stars in Space.*" By Prof. F. W. Dyson, F.R.S.

"*Conditions Necessary for Discontinuous Motion in Gases.*" By G. I. Taylor.

"*The Radium Content of Basalt.*" By the Hon. R. J. Strutt, F.R.S.

"*Measurements of the Rate at which Helium is produced in Thorianite and Pitchblende, with a Minimum Estimate of their Antiquity.*" By the Hon. R. J. Strutt, F.R.S.

PHYSICAL SOCIETY.

Ordinary Meeting, November 11th, 1910.

Prof. H. L. Callendar, F.R.S., President, in the Chair.

A Paper "*On the Supposed Propagation of Equatorial Magnetic Disturbances with Velocities of the Order of 100 Miles per Second,*" was read by Dr. C. Chree.

The question of the simultaneity of magnetic disturbances recorded at different stations has recently been discussed by Dr. Bauer and Mr. Faris. A good many magnetic storms have so-called "sudden commencements." As regards these "sudden" changes three things are conceivable; they may be absolutely simultaneous at different stations; there may be a very small difference of time corresponding to the rate of propagation of electromagnetic waves; or, finally, there may be, as Dr. Bauer concludes, longer intervals, amounting to several minutes, for stations remote from one another. Dr. Bauer concludes that Mr. Faris's figures demonstrate the truth of his theory that disturbances normally are propagated round the earth, sometimes eastward sometimes westward, the time of a complete revolution averaging about three and three-quarter minutes. The author of the present paper discusses the weaknesses of Dr. Bauer's theory. He points out that the theory could be adequately tested by a careful comparison of curves from selected stations fairly encircling the globe, choosing if possible stations whose time-measurements are specially reliable.

A paper entitled "*On Cusped Waves of Light and the Theory of the Rainbow,*" was read by Prof. W. B. Morton.

Diagrams were shown of the forms assumed by a plane-wave of light falling on a spherical raindrop and twice reflected from the interior of the drop, as well as the waves emerging from the drop. The waves in general have cuspidal edges which run along the caustic surfaces. This relation between the caustic and the cusps on the waves was pointed out by Wood in connection with the similar waves produced by reflexion at a spherical surface. It had been noticed earlier by Potter, Jamin, and Macé de Lepinay. The phase over a wave of this type is not constant, the two portions on opposite sides of a cusp differing in general by a quarter period. Attention was drawn to the advantage of regarding the distribution of light in the rainbow as the consequence of the interference of the cusped waves which run down to the observer's eye along the direction of minimum deviation. This way of looking at the matter is shown to be equivalent to Mascart's approximate method of explanation of the formation of the supernumerary bows by interference of disturbances coming from the two poles on the special wave-form used by Airy.

Prof. C. H. Lees pointed out that the boundary of the disturbance as it passed through the drop would be subject to diffraction effects. He asked if this would make any material difference in the results arrived at in the paper.

The Author, in reply, stated that diffraction phenomena would not seriously affect the diagrams he had obtained.

NOTICES OF BOOKS.

Metropolitan Water Board. Fourth Annual Report and Fifth Research Report. By Dr. A. C. HOUSTON.

THE fourth annual report of the Metropolitan Water Board gives in detail the results of the chemical and bacteriological examination of the London waters for the twelve months ending March 31, 1910, and summarises the chief conclusions to be drawn from them. The fifth report on Research work contains the reports of the examination of samples of raw Thames and other water for various bacilli, the results of the examination of the Pre-filtration water, and other important data.

The Extra Pharmacopœia of Martindale and Westcott. Revised by W. HARRISON MARTINDALE, Ph.D., F.C.S., and W. WYNN WESTCOTT, M.B. (Lond.), D.P.H. Fourteenth Edition. *Organic Analysis Chart.* By W. HARRISON MARTINDALE. Supplement to the Extra Pharmacopœia, Fourteenth Edition. London: H. K. Lewis. 1910.

THE new edition of the Extra Pharmacopœia has been issued in two volumes, the second of which contains a complete organic analysis chart; this gives sufficient information for the identification of all organic substances, both natural and synthetic, which are used therapeutically, Over 300 such substances are included, and the data have practically all been obtained or verified in the author's own laboratory, so that the physical constants and the details of the tests may be regarded as undoubtedly trustworthy. The first volume contains the text of the thirteenth edition, together with new articles on various important subjects, such as lactic acid bacilli therapy, organic arsenic compounds, and radium. Many new preparations are now described for the first time, and, moreover, considerable additions have been made to the number of patent medicines and proprietary articles, of which analyses are given.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académié des Sciences. Vol. cli., No. 14, October 3, 1910.

Organic Compounds of Tetravalent Tellurium.—Charles Lederer.—Phenyl telluride, $(C_6H_3)_2Te$, can be prepared by adding tellurium tetrachloride to an ethereal solution of phenyl magnesium bromide. When its aqueous solution is heated with potassium iodide triphenyl-telluronium iodide, $(C_6H_5)_3TeI$, is obtained, and can be converted into the corresponding chloride or bromide by double decomposition with a boiling suspension of silver chloride or silver bromide. Besides this type of tetravalent compounds of tellurium there is another series containing two atoms of halogen, *e.g.*, $(C_6H_5)_2TeBr_2$, while a third series may be prepared by the addition of hydracids to phenyl telluride; thus with hydrochloric acid the compound $(C_6H_5)_2TeHCl$ is obtained.

Action of Quinones and their Sulphonic Derivatives on Silver Salt Photographic Images.—A. and L. Lumière and M. Seyewetz.—In acid solution benzoquinone and its sulphonic derivative can be used to reduce photographs obtained with silver salts. In alkaline solution they act as intensifiers, and apparently they will be found valuable reagents in photography. Quinone is the first organic compound possessing these properties, and no inorganic compound can be used similarly.

MISCELLANEOUS.

Obituary.—At Sutton-on-Hull, on the 20th inst., Lewis Edward Common, Chemist of the Hull Oil Manufacturing Co., Ltd.

Salts of Tin in Food.—The attention of the United States Department of Agriculture has been directed to canned goods which contain salts of tin derived from the solvent action of the contents of the package upon the tin coating. Pending further investigations on this question all canned goods which are prepared prior to January 1, 1911, will be permitted to enter and pass into interstate commerce without detention or restriction in so far as their content of tin salts is concerned. All foods which are canned subsequently to January 1, 1911, will be permitted importation and interstate commerce if they do not contain more than 300 mgrms. of tin per kilogrm., or salts of tin equivalent thereto. When the amount of tin, or an equivalent amount of salts of tin, is greater than 300 mgrms. per kilogrm., entry of such canned goods packed subsequently to January 1, 1911, will be refused, and if found in interstate commerce proper action will be taken. It is the opinion of the Board that the trade will experience little hardship in adjusting itself to this condition, as the results of examinations made by the Bureau of Chemistry of various types of canned goods indicate that in a very large majority of cases inconsiderable quantities of tin are found, well within the limit herein set.

NOTES AND QUERIES.

"*" Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Reducing Acetylene to Amorphous Carbon.—While making investigations into the construction of a simultaneous generating and storing tank for acetylene, a property heretofore unknown revealed itself to me. The head of this tank consists of a stopcock and a long nipple. Before sealing the tank it was filled with calcium carbide; then water was poured into the nipple and admitted by opening the stopcock. Before all the water had left the tube some gas was generated and bubbled up through the nipple. A lighted match was held at the mouth of the tube. As the bubbles of gas were emitted they exploded violently. The explosion took place so quick that the flame was hardly visible. As the bubbles exploded a ring of amorphous carbon floated up through the air. The only explanation that I can satisfy myself with, is that the explosion was so quick that the heat generated was dissipated before it could convert the carbon into carbon dioxide.—FRANCIS B. COYLE.

MEETINGS FOR THE WEEK.

MONDAY, 28th.—Royal Society of Arts, 8. (Cantor Lecture). "Industrial Pyrometry," by C. R. Darling.

TUESDAY, 29th.—Royal Society of Arts, 4.30. "Progress and Prospects of Mining in Western Australia," by A. Montgomery, M.A., F.G.S.

WEDNESDAY, 30th.—Royal Society of Arts, 8. "Argentina from a British Point of View," by C. P. Ogilvie.

THURSDAY, Dec. 1st.—Chemical, 8.30. "The Triazo-group—Part XV., Triazoethylene (Vinylazoimide) and the Triazoethyl Halides," by M. O. Forster and S. H. Newman. "Determination of Solubility Coefficients by Aspiration," by W. J. Jones. "Auto-reduction of Hydrazines," by F. D. Chattaway and M. Aldridge. "Nitro-derivatives of Dimethyl-*p*-toluidine," by G. T. Morgan and A. Clayton.

CHEMICAL SOCIETY RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in DECEMBER next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary of the Society, Burlington House, W., must be received on or before MONDAY, DECEMBER 5th, 1910.

The Council wish to draw attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of Research in Inorganic and Metallurgical Chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the Coal-tar and allied Industries.

THE CHEMICAL NEWS.

Vol. CII., No. 2662.

REPORT ON GASEOUS COMBUSTION.*

By WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S.

(Continued from p. 262).

Section II.—*The Explosion Wave.*

Bertholet and Vieille, in announcing their discovery of the development of detonation ("l'onde explosive") in gaseous explosions (*Ann. Chim. Phys.*, 1881, [5], xxviii., 289), described it as "une certaine surface régulaire, où se développe la transformation, et qui réalise un même état de combinaison, de température, de pressure, &c. Cette surface, une fois produite, se propage ensuite, de couche en couche, dans la masse tout entière, par suit de la transmission des chocs successifs des molécules gazeuses amenées à un état vibratoire plus intense en raison de le chaleur dégagée dans leur combinaison, et transformées sur place, ou, plus exactement, avec un faible déplacement relatif. . ." Such conditions are comparable with those of a sound wave passing through the gaseous mixture, with, however, the important difference that, whereas a sound wave is propagated from layer to layer with a small compression and a velocity determined solely by the physical condition of the vibrating medium, it is an abrupt change in chemical condition which is propagated in the explosion wave, and which generates an enormous force as it passes through each successive layer of the medium. Berthelot considered that the mean velocity of translation of the molecules of the products of combustion, retaining the total kinetic energy corresponding to the heat developed in the reaction, may be regarded as the limiting maximum rate of propagation of the explosion wave (θ), which would be given in metres per second by the equation—

$$\theta = 29{\cdot}354\sqrt{\frac{T}{\rho}};$$

where T is the absolute temperature and ρ the density of the products referred to air. In calculating T, Berthelot made two erroneous assumptions—namely, (1) that the specific heats of the products are independent of temperature and equal to the sum of the specific heats of the reacting gases, and (2) that the gases burn under conditions of constant pressure. He was also of opinion that, owing to the high pressure generated, dissociation plays no appreciable part in the phenomena of the wave.

In their experimental work Berthelot and Vieille proved that the velocity of the explosion wave is independent of the length of the column of gas traversed, and of the material or diameter of the tube employed (at least above a certain small limiting diameter). It was also immaterial whether the tube was laid out straight, coiled round a drum, or even zigzagged. They also concluded that the velocity is independent of the initial pressure, but this is not strictly correct, as H. B. Dixon has since shown. The rate increases slightly with the initial pressure, attaining a nearly constant value at a pressure of about 2 atmospheres.

H. B. Dixon, the bearing of whose researches upon the question of the mechanism of combustion will be discussed later, modified Berthelot's theory in the following particulars (the reader is referred to the original memoir in the *Phil. Trans.*, 1893, clxxxiv., 97, for the details of the argument), namely, by assuming (1) that the explosion wave is carried forward by movements of molecules of density intermediate between that of the products of combustion and that of the unburnt gas; (2) that the gases are heated at constant volume; (3) that the temperature of the gas propagating the wave is double that due to chemical reaction alone; (4) that the temperature is increased when the chemical volume of the products is larger, and diminished when it is smaller, than that of the unburnt gases; and (5) that the velocity of a sound wave is only 0·7 of the mean velocity of the molecules in the gas. Dixon's formula for the rate of explosion of a given mixture is, therefore, as follows:—

$$v = 0{\cdot}7 \times 29{\cdot}354\sqrt{\left(\frac{2Q}{Cv} + T\right)\left(\frac{v_2}{v_1}\right)^{\varkappa - 1}}{\rho}$$

where Q = the heat developed by the reaction, v_2 and and v_1 = the chemical volumes of the products and unburnt gases respectively, ρ = the mean density of the products and the unburnt gases, and Cv = the specific heat of the products at constant volume, which Dixon wrongly assumed to be independent of the temperature, T = the temperature in C°, and $\varkappa$ = the ratio of the specific heats.

But, whereas the values of v, calculated by this formula, do in many instances correspond with those actually found (*e.g.*, for mixtures of cyanogen and oxygen, and in nearly all cases where the detonating mixture is largely diluted with an inert gas), there are a large number of cases of undiluted detonating mixtures in which the agreement is not good (*e.g.*, for $2H_2 + O_2$ the calculated value is 3116, whereas that actually found is only 2821 metres per second). Dixon ascribed such discrepancies to the partial dissociation of the products in the wave, but there is now little doubt that the formula does not hold good, as Dixon himself readily enough admits (see his recent Presidential Address to the Chemical Society, *Trans. Chem. Soc.*, 1910, xcvii., 665). Nevertheless for many years it was a valuable working hypothesis and inspired much fruitful investigation.

In 1899 D. L. Chapman, following up a suggestion made by Schuster at the time when Dixon's memoir was published (*loc. cit.*, p. 152), deduced a formula for rates of explosion from Riemann's equation for the propagation of an abrupt variation in the density and pressure of a gas, on the assumption that such a variation can be propagated without change of type (*Phil. Mag.*, 1899, p. 90). According to this view the explosion wave is to be regarded as a wave of compression not in a homogeneous medium, but in a medium which is discontinuous in the vicinity of the wave-front. It is assumed (1) that the "front" of the wave (*i.e.*, from the unexploded gas to the point of maximum pressure) does not alter in character, or, in other words, that every portion of the wave travels with the same velocity; (2) that the velocity is the minimum velocity consistent with (1); and (3) that at the point of maximum pressure the chemical change concerned in the propagation of the wave is complete. The unburnt gases immediately in front of the waves are, of course, fired by compression, and the abrupt variation in the density and pressure of the medium is due to the chemical change. Chapman's formula for the velocity of the explosion wave in centimetres per second is—

$$V = \sqrt{\frac{2RJ}{\mu C_v^2}\left[\tfrac{1}{2}(m-n)C_p + mC_v\right]C_p t_0 + (C_p + C_v)h},$$

where R = the gas constant (1·985), J = the dynamical equivalent of heat (42×10^6 ergs), μ = the grm. equivalents of the mixture exploded (*e.g.*, 58 in the case of $C_2H_2 + O_2$), n and m = the number of gaseous molecules before and after the chemical change in the wave, C_p and C_v = the mean specific heats of the products at constant pressure and volume respectively, h = the total heat generated in the wave, and t_0 = the initial temperature (abs.) of the mixture exploded. From the fact that the dilution of electrolytic gas ($2H_2 + O_2$) with oxygen lowers its rate of explosion a little more than a corresponding dilution with nitrogen, Chapman considers it improbable that there is any appreciable dissociation of steam in the

* Read before the British Association (Section B), Sheffield Meeting, 1910.

Table A.

Mixture.	*h*.	*m*.	*m*−*n*.	μ.	C*v*.	Temp.	A.	B.	V. in metres per second. Calculated.	Found.
H_2+N_2O	152,500	4	0	92	10·81	3813°	15,640	3,758,750	2425	2305
$H_2+N_2O+2H_2$ ..	152,500	6	0	96	9·10	3077°	20,980	3,251,500	2612	2545
$H_2+N_2O+2N_2$ ..	152,500	6	0	148	9·10	3077°	13,610	3,251,500	2104	1991
$H_2+N_2O+2O_2$ ..	152,500	6	0	156	9·10	3077°	12,830	3,251,500	2042	—

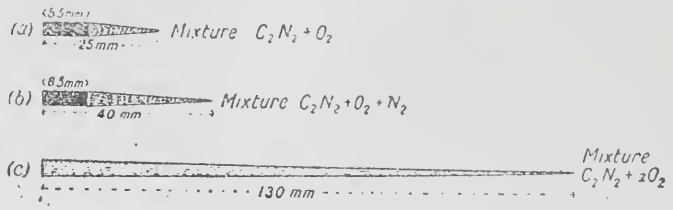


Fig. 2.

wave. He assumes that the molecular heat of steam rises more rapidly with temperature than that of a diatomic gas, and that the molecular heats of oxygen, hydrogen, nitrogen, and carbon monoxide may for all practical purposes be considered as equal at any given temperature. Selecting some seventeen of Dixon's found rates of explosion, he has calculated by means of his formula the corresponding molecular heats and temperatures, arriving at the following results for C*v* at intermediate temperatures by interpolation :—

Temperature.	C*v*. Steam.	C*v*. Diatomic gases.
4300°	14·750	7·707
4000	14·297	7·674
3700	13·750	7·641
3400	13·102	7·608
3100	12·250	7·575
2800	11·040	7·542
2500	9·797	7·509

With the aid of this series of numbers he proceeded to apply his formula to the calculations of the rates of explosion of some forty other mixtures investigated by Dixon, finding in all cases close agreement between the found and calculated values, of which the following may suffice as examples :—

Mixture exploded.	Products in the wave.	Temp.	Rate of explosion. Metres per sec. Calc	Found.
$2H_2+2N_2O$	$2H_2O+2N_2$	3813°	2408	2305
$4H_2+2N_2O$	$2H_2O+2N_2+2H_2$	3077	2604	2545
$6H_2+2N_2O$	$2H_2O+2N_2+4H_2$	2612	2720	2705
$2H_2+2N_2O+2N_2$	$2H_2O+4N_2$	3077	2097	1991
$C_2H_4+2O_2$	$2CO+2H_2O$	4365	2619	2581
$C_2H_4+3O_2$	$2CO+2H_2O+O_2$	3882	2348	2368
$C_2H_2+O_2$	$2CO+H_2$	5029	3101	2961
CH_4+O_2	$CO+H_2O+H_2$	2772	2502	2528
$2CH_4+3O_2$	$2CO+4H_2O$	3764	2485	2470
$2CH_4+3O_2+N_2$	$2CO+4H_2O+N_2$	3513	2353	2349

A characteristic feature of detonation is the extremely short duration of chemical action and subsequent rapid cooling of the products, as compared with ordinary combustion. Some years ago the writer, working in conjunction with Bevan Lean, under Prof. H. B. Dixon's direction, found by a photographic method that the duration of luminosity in each successive layer of gas in the detonation of electrolytic gas is certainly less than 1/5000 second (*British Association Reports*, 1892), a much shorter interval of time than was required to shatter a tube of thin glass attached to the end of the explosion coil used. This tube, although invariably smashed by the force of the explosion, always appeared perfectly intact in the photograph. Dixon's subsequent photographic researches have demonstrated the abrupt suddenness with which the gases attain the maximum temperature in detonation, the intensity and short duration of luminosity, and the subsequent rapid cooling, as compared with ordinary combustion. Moreover, high as is the temperature attained, there is no evidence of any considerable dissociation of steam in the wave, for, despite the instantaneous cooling of the products, there is less than 1 per cent of the gases left uncombined after the wave has passed through electrolytic gas, $2H_2+O_2$.

Influence of an Excess of an Inert Gas upon the Rate of Explosion.—Writing Chapman's formula as follows :—

$$V^2 = \frac{2RJ}{\mu C_v{}^2}\left[\{(m-n)C_p + mC_v\}\,C_p t_o + (C_p+C_v)h\right],$$

and putting $\frac{2RJ}{\mu C_v{}^2} = A$, and the terms between the square brackets = B, it will be immediately perceived that the addition of an inert diatomic gas (*e.g.*, H_2, N_2, or O_2) to a given explosive mixture will affect the values of both A and B, but not necessarily in the same direction. It will increase the value of μ and diminish the values of C*v* and C*p*, partly by lowering the temperature in the wave and partly also (if steam or carbon dioxide be formed in the wave) by reason of its own specific heat being lower than that of the undiluted products. It will also increase the value of *m* without altering (*m* − *n*). If it be assumed that the molecular heats of the three diatomic gases under consideration are, for all practical purposes, equal at any given temperature, it will be at once seen that an equal dilution of a given explosive mixture with any one of the three gases, whilst it will have an equal effect on all terms included under B, may either increase or diminish the value of A, according as to whether or not the *plus* effect of the lower value of C*v* is counterbalanced by the *minus* effect of the increase in μ. If the latter effect be small, as would be the case with hydrogen as diluent, the value of A would on the whole be increased; whereas if the increase in μ were large, as would be the case with nitrogen or oxygen as the diluent, the value of A would on the whole be diminished.

As an example of the probable effects of the equal dilution of a given explosive mixture with each of the three gases in question, the case of an equimolecular mixture of hydrogen and nitrous oxide, fired at 10° and 760 mm., may be cited. (See Table A).

An inspection of the figures under columns A and B will at once make it clear why, whereas dilution with hydrogen is invariably found to increase the rate of explosion of a given mixture, an equal dilution with nitrogen or oxygen invariably diminishes it, and also why the retarding influence of oxygen must always be greater than that of an equal proportion of nitrogen. The following examples,

taken from Dixon's memoir, may be cited in support of the above argument :—

Effects of Dilution upon the Rate of Explosion of Electrolytic Gas.

Mixture Exploded.	Rate. Metres per second.
$2H_2+O_2$	2817
$2H_2+O_2+2H_2$	3268
$2H_2+O_2+4H_2$	3527
$2H_2+O_2+6H_2$	3532
$2H_2+O_2+O_2$	2328
$2H_2+O_2+3O_2$	1927
$2H_2+O_2+N_2$	2426
$2H_2+O_2+3N_2$	2055

Effects of Dilution with Hydrogen upon the Rate of Explosion of Hydrogen and Chlorine.

Mixture	H_2+Cl_2	$2H_2+Cl_2$	$3H_2+Cl_2$
Rate ..	1729	1849	1855 metres per sec.

The Burning of Gaseous Carbon.—Of the many important facts brought to light during the course of Dixon's investigation none are of greater interest than those relating to the burning of gaseous carbon in the explosion wave, as illustrated by the case of cyanogen. In view of the fact that the molecular heat of combustion of cyanogen, when burnt completely to carbon dioxide, is 259·6 kilogrms. C. units, whereas, if burnt to the monoxide it would only be 123 units, it might be expected that the rate of explosion for a mixture $C_2N_2+2O_2$ would be much higher than for $C_2N_2+O_2$, if gaseous carbon is primarily burnt to carbon dioxide in the wave. The exact opposite is the case, however, as the following results show :—

Mixture.	Products.	Rate.
$C_2N_2+O_2$	$2CO+N_2$	2728 metres per sec.
$C_2N_2+2O_2$	$2CO_2+N_2$	2321 ,,

Still more cogent is the evidence in favour of the initial formation of carbon monoxide in the wave, when the following figures are considered :—

	$C_2N_2+O_2$	$C_2N_2+O_2+N_2$	$C_2N_2+O_2+O_2$
Rate..	2728	2398	2321

The conclusion to be drawn from the preceding figures is that cyanogen is initially burnt to carbon monoxide and nitrogen in the wave itself, any excess of oxygen afterwards burning up the carbon monoxide as the gases cool down in the rear of the wave.

This conclusion was driven home by Dixon, in conjunction with Strange and Graham, by photographing on a sensitive film, rotated at a speed of about 1500 m. per minute, the explosion flame in the case of the three mixtures (*a*) $C_2N_2+O_2$, (*b*) $C_2N_2+O_2+N_2$, and (*c*) $C_2N_2+2O_2$. In each case the flame was photographed, after detonation had been set up, as it dashed past a glass window inserted into the lead explosion coil (*Trans. Chem. Soc.*, 1896, lxix., 759). The image obtained in the case of (*a*) showed an intensely brilliant flame (the explosion wave), slightly drawn out in tapering form; in the case of (*b*), with nitrogen as diluent, the flame was less brilliant and somewhat more drawn out than in (*a*); but with (*c*) the flame, whilst no more luminous than in (*b*), was drawn out to great length, owing to the continued combustion of carbon monoxide in the rear of the wave. The diagram, Fig. 2 (approximately to scale), will convey an idea of the relative durations of the flames in the three cases.

The Burning of Hydrocarbons in the Wave.—It was during the course of measurements of the rates of explosion of hydrocarbons with varying proportions of oxygen in 1891-92 that Dixon and his collaborators re-discovered facts (originally set forth by Dalton in his "New System of Chemical Philosophy") which finally disposed of the dogma that in a deficient supply of oxygen a "selective" burning of hydrogen occurs. It was found that when either ethylene or acetylene is detonated with its own volume of oxygen the ultimate products consist almost entirely of carbon monoxide and hydrogen (*vide* Lean and Bone, *Trans. Chem. Soc.*, 1892, lxi., 873; and Bone and Cain, *Trans. Chem. Soc.*, 1897, lxxi., 26). The rates of explosion, whilst they do not reveal the real mechanism of the combustion, show very clearly that, as in the case of cyanogen, the carbon of a hydrocarbon is burnt initially to the monoxide in the wave itself, the formation of the dioxide being an after effect and taking place in the rear of the wave. In the cases of methane and acetylene the fastest rates are observed with equimolecular mixtures, whereas with ethylene the rate increases with the proportion of oxygen up to the limit $C_2H_4+2O_2$. As the question of the mechanism of hydrocarbon combustion will be fully discussed later, the following rates of explosion, as determined by Dixon, may now be given without further comment :—

(A) *Methane and Oxygen in varying Proportions, Fired at 10° and 760 mm.*

Mixture	Rate. In metres per second.
CH_4+O_2	2528
$CH_4+1\frac{1}{2}O_2$	2470
CH_4+2O_2	2322
CH_4+3O_2	2146 (*a*)
CH_4+4O_2	1963

(B) *Ethylene and Oxygen in varying Proportions, Fired at 10° and 760 mm.*

$C_2H_4+O_2$	2507
$C_2H_4+2O_2$..	2581
$C_2H_4+3O_2$..	2368 (*b*)
$C_2H_4+4O_2$..	2247
$C_2H_4+6O_2$..	2118

(C) *Acetylene and Oxygen in varying Proportions, Fired at 10° and 760 mm.*

$C_2H_2+O_2$	2916
$C_2H_2+1\frac{1}{2}O_2$	2716
$C_2H_2+2\frac{1}{2}O_2$	2391 (*c*)

(*a*) Compare this with the 2154 metres per second observed for $CH_4+1\frac{1}{2}O_2+1\frac{1}{2}N_2$ as showing the inertness of at least the moiety of the oxygen in the wave.

(*b*) Compare this with the 2413 metres per second observed for $C_2H_4+2O_2+N_2$.

(*c*) Compare this with the 2414 metres per second observed for $C_2H_2+1\frac{1}{2}O_2+N_2$.

(To be continued).

Preparation of Aromatic Alcohols and their Acetates.—A. Wohl and E. Berthold.—Bromphenetol can be prepared by the action of sodium phenolate on ethylene bromide, but the yield is poor. If, however, the ethylene bromide is treated with aqueous phenolate, and if the phenol salt is added gradually, the yield is much increased. The bromphenol esters obtained with phenol, guaiacol, and eugenol, when heated with solid powdered potash, give phenol vinyl ether and phenol ethylene ether. ω-Phenyl-phenetol can be prepared by Grignard's method if the ether is distilled off *in vacuo* from the bromphenyl magnesium solution, and the mixture is then heated to boiling for forty-eight hours with xylol. To convert the phenyl esters into acid esters it is best to boil with acetic acid in presence of sulphuric acid.—*Berichte*, xliii., No. 12.

BANQUET TO PAST-PRESIDENTS OF THE CHEMICAL SOCIETY.

NOVEMBER 11, 1910.

(Continued from p. 253).

THE following further speeches were delivered in response to the toast of the "Past-Presidents who have been Fellows for Half-a-Century":—

Dr. HUGO MÜLLER.

My colleagues have already given expression to the reminiscences and sentiments which suggest themselves most prominently on this festive occasion, and I feel there is but little for me to add on my part.

I have been connected with this Society for over fifty years, for I was a constant attendant at the meetings from as early a date as 1854, when I was an Associate; later, in 1859, I was elected a Fellow.

It is eminently satisfactory to have been connected with so prosperous a concern, and still more so when one has had some small share in its development and administration.

Our Society, which was the first of its kind and became afterwards the prototype of many others, was then still in its infancy, and the slender volumes of the *Quarterly Journal* then published give some idea of the limited extent of its activity. Sometimes there was actually a dearth of material, and appeals were occasionally made to members to furnish some matter for communication at the meetings. However, in those days the meetings used to be taken up much more with the discussion of the papers than is the case now-a-days, when chemical research has become so intensely specialised and consequently affords fewer opportunities for spontaneous discussion.

At that period the Society met at rooms in Cavendish Square connected with the premises of the Polytechnic in Regent Street.

Our Society made, however, such steady progress that by the time we were located in Burlington House it had already attained a large membership, and had grown more and more flourishing, and had become indeed of decided importance.

Probably it was mainly on this account that now some of the members became very anxious to introduce certain alterations in the character of the Society, with the object of giving the Fellowship a more professional status, and the consequent perturbation was a very serious matter for those who were in charge of affairs, and this state of things lasted for some years.

Ultimately it found vent in the formation of the Institute of Chemistry, the Society of Chemical Analysts, and the Society of Chemical Industry.

When at the present day we contemplate the varied activities of all these offsprings of our Society, we recognise the utter impossibility of comprehending them within the scope and aim of the parent society, and you will agree with me that it is a matter of congratulation that we have successfully resisted this agitation for a change in its constitution.

We may fairly consider the contents and size of our *Transactions* as a measure of the flourishing condition and great importance of our Society. It is also a satisfactory feature and well worth mentioning that the cost of our publications is still fairly balanced and within our income, for it is quite conceivable that at some future period the communication of papers will become so numerous and their publication so costly that the subscription of the Fellows may no longer suffice to cover the expenses, a contingency which at present is actually causing considerable trouble to one of our sister societies.

In conclusion, I beg to offer you my hearty thanks for the great honour you have done us in providing this splendid entertainment.

Mr. A. G. VERNON HARCOURT.

Probably each one of us five regards the period in which he held office as a particularly important time; nor can I claim to be free from this impression. It was while I was a Secretary of the Society that we made place for the Artists, and left our apartment at the east end of old Burlington House to move into the less secluded but ampler quarters which we now occupy. On the day on which I became President, our Faraday Medal was presented by my predecessor, Dr. Armstrong, to Lord Rayleigh for the discovery of argon, resulting from his observation of the different densities of atmospheric and chemically prepared nitrogen. In the separation and investigation of argon, Lord Rayleigh worked with Prof. Ramsay, and the award of the medal was immediately followed by the announcement by Prof. Ramsay of another gaseous element, helium, which, like argon, had been mistaken for nitrogen, and which had been discovered as a constituent of the atmosphere of the sun before it had been recognised on earth and found to be a constituent of our own atmosphere. The actual measurements of the spectrum of the new element and the identification of the gas from cléveite with the helium of the sun were then communicated to the Society by one of our Past-Presidents, Sir William Crookes. Two years later, when Prof. Ramsay had made a complete investigation of the mineral sources and properties of helium, I had the pleasure of presenting to him the Longstaff Medal.

Many other important communications were made to the Society during those two years, and we listened to the memoirs of three great men of science—Helmholtz, Lothar Meyer, and Pasteur. But that was more than thirteen years ago, and the thirteen years between the ages of sixty-three and seventy-six make a great difference to a man; and I must hope that our proceedings at that time are better retained in the memories of many of my audience than they are in my own.

There used to be a yearly cricket match, in which the players were Chelsea Pensioners, all old men, if not all over seventy, with the further disadvantage, which is not shared by your guests to-night, that half of them had only one arm, and the other half only one leg. It would be unjust to those who arranged the match and gave dinner to the players to put among their motives the fun of trotting the old boys out, or to doubt that they watched their efforts with kindly and uncritical eyes. Fortunately your veterans are not called upon to do anything of an active kind—not even to show manipulative skill—but only to acknowledge and thank you for the kind feeling and the wish to do them honour which have brought us here.

One cannot help putting to oneself the question: What have we done more than other Past-Presidents of the Society to gain this honour? All right-minded men, who are free from severe pain or grief, enjoy life, and wish it to be prolonged. What others cherish and desire, we have achieved; nor, even at this culmination of our careers, do we ask now to be dismissed, but appear before you—to use Charles Lamb's phrase—as "jolly candidates" for the second decade of the century.

It is said that Faraday as age advanced upon him found that his memory was failing, and that he must choose for investigation some wholly new subject, not requiring any recollection of previous work; and it is said further that to this limitation was due the discovery of diamagnetism. Ordinarily, such failure of memory has a less satisfactory result. An old man may retain his interest in the parts of science which most attracted him, but of what he reads little remains a few days later, and he gradually desists from that study of the current literature of science which to younger men is both an enjoyment and a necessary condition of useful work. I have an intimate and rather painful knowledge of one such case; but I may be generalising too hastily, for some of your old Past-Presidents are able to bring their long experience to bear upon the present, and to make shrewd and illuminating

remarks upon the recent progress of chemistry. I, unfortunately, am only conscious that our science is advancing and changing with bewildering speed.

Conjectural formulæ, presumably well founded, contend with one another. I remember that the constitution of camphor was being settled when I was President, and that rival formulæ received vigorous support. In the explanation of chemical changes and of the structure of molecules, human ingenuity is more than a match for the complexity of nature. When, as must happen occasionally, a hypothesis is punctured by collision with some hard fact, it is at once neatly patched with another hypothesis. The atoms in which we believed, and the molecules which passed into solution entire or flitted about as gases, are now broken up into much smaller pieces. Chemists discovered the formation of ions, independently of an electric current, and the Physicists presented them with electrons. Elements gradually disappear, at fixed rates, in a certain number of years or even of days. Our foundations are shaken; and one may fear that fifty years hence, when some of our youngest Fellows will be Past-Presidents enjoying their jubilee, the very hexagon may have lost its place of honour in chemical literature.

In this connection I will venture to refer to a question of some public importance with which chemists have to deal, namely, the influence of the rapid growth of Chemistry, and especially of chemical views—which my good friend and master, Sir B. Brodie, called "Ideal Chemistry"—upon the teaching of the science as a part of general education.

We shall most of us agree that after reading, writing, and arithmetic, and next in value to moral instruction, comes a knowledge of the general results of scientific inquiry and some insight into the methods by which such knowledge has been gained. What parts of chemistry should find a place in such a scheme? Two limitations may be suggested, first, to facts and generalisations which are absolutely established; and secondly, to familiar substances, the chemistry of common life. The enthusiastic chemist, who aims at keeping himself abreast of his subject, and to whom the teaching of chemistry, not only to future chemists, but as a part of general education, is rightly entrusted, must find it more and more difficult to make the necessary "cuts." He has to bear in mind that however valuable the latest hypotheses may be for the progress of chemistry or for the advanced student who has an examination to pass, they must not be put before those who are only studying science as a part of education and chemistry as a part of science, and who may be misled into thinking that they are well forward in chemistry because they have gained some of the latest lights.

We older chemists are often told that the amount of chemistry which has to be learnt for examinations now, is far greater than was required in our time. I do not believe it. The average of industry and of memory, the two great factors in the storage of knowledge, does not change much in fifty or sixty years. The things taught are different. Much is added, and therefore much has to be omitted. Fifty years hence there will be the same disposition of those who are in the front to speak scornfully of what is being taught now.

This line of reflection brings us to the oppressive thought, which must not be too much indulged, of the littleness of our steps forward in science compared with the immensity of what there is to be known.

> "We have not gained a real height,
> Nor are we nearer to the light,
> Because the scale is infinite."

I must not end this evening on so sad a note. The same fact may be looked at quite otherwise. It is the successful, or even the unsuccessful, pursuit of truth which gives happiness to each generation of scientific men, and not the value of the truth itself—the energy, the doing, not the thing done. If a time could arrive, when all was known, when there could not be a new investigation or experiment, our keenest pleasure would be at an end. We may therefore feel happy in the thought of how much is still unknown. The questioning of nature is likely to last as long as the generations of mankind.

It only remains for me, in conclusion, to thank you, gentlemen, and especially my friend our President and the members of the Council, for my share in the honour and the pleasure which you have bestowed upon your old Past-Presidents.

Prof. William Odling.

From my point of view, the most important thing I have to say is to express to you my appreciation and deep gratitude of the honour you have done me. This is the third occasion on which I have been entertained publicly at the hands of the Society. In this respect, I feel I cannot express myself in words better than those you have already heard read from the letter sent by Sir Henry Roscoe.

It is a great gratification to us seniors to feel we are not altogether forgotten. We greatly appreciate the kind feeling which still attaches to us in memory of old days. If it only depended upon myself, I think I could go on for a very long time talking of the old days, but it is a question whether it would interest some of you. On a previous occasion—twelve years ago—I was honoured in a similar manner at an entertainment which was presided over by my successor—my almost immediate successor at the Royal Institution—Sir James Dewar, who has so worthily filled the position he now holds, and who has achieved for himself a world-wide reputation. I was at that time associated with five of my very oldest friends. At the present time I am associated with others of almost as long standing, and I will venture to express a word or two with regard to each of them, not in their abstract but in their personal relations with me. I can only express regret that their number is now four. What pleasure it would have given us to have included in our numbers Perkin and Russell. Both were distinguished as chemists—one of them as a pioneer—and both of them were estimable and lovable in character, and devoted to the interests of the Society. With regard to Roscoe, he was seven years my junior as a Fellow of the Society, and seven years my junior as a President.

He always had a very youthful appearance, and I can at this moment remember making his acquaintance in Williamson's laboratory. Williamson introduced Roscoe to me as one of his most promising pupils. In expressing my appreciation of the great personal attractiveness of Williamson, I must say that those who have only known him in later years can have no conception of the magic of his influence on those who were thrown into association with him.

My acquaintance with Crookes has been hardly so long as with Roscoe, but, at any rate, it has been equally close; more close, in fact, for a number of years. I am delighted, on an occasion such as this, to be associated with Crookes as one of our guests this evening. He is as active as ever. Forty years ago, when I was a member of the Council of the Royal Society, I had a paper sent to me, and I had to say whether it was meritorious enough to be published. It was on the atomic weight of thallium. I will not say what was the nature of my report, beyond that the paper was published. But I would venture to say that the publication of that paper marked an era in this country in the determination of atomic weights—I can almost say in any country. Even with regard to the work of my old friend Stas, it was its equal, if not superior. I do not know how many of you will remember Stas. He was affectionate and effusive in his demonstrations. I met him at the door of the International Exhibition of 1862, and, knowing his effusiveness, I held back a little. But in a minute or so he had laid hold of me, put his arms around my neck, and kissed me on the cheek, to the consternation of a burly policeman standing near.

As a lecturer on organic chemistry, it is surprising to me to find how constantly I had to refer to the researches of Dr. Müller. We esteem him for his con-

tributions to science, and, above all, for his personality and amiable character, which has endeared him to all of us. I have an additional obligation, for it was through him that I became known to and associated with Kekulé, a name always to be mentioned with honour in the study of organic chemistry.

Harcourt and I have been associated as teachers at the University, and although not always seeing a thing from the same point of view, we have in the main agreed, always feeling that there existed a pleasant relationship one to another. To Harcourt we are all indebted for his history of the formation of the University Museum, an institution which has done so much for the advancement of science at Oxford. It has done great things for the study, not only of chemistry, but of natural science generally at Oxford, and this brings me to say a word or two about the association of Oxford with the Chemical Society. Fifth in order of the series of Presidents was Dr. Daubeny, who was at that time professor, and whose memory is still dear to Oxford men and is embodied in the Daubeny laboratory. He was President of the Chemical Society, and among the twenty-seven of his successors we find four other Oxford teachers. He was followed by Brodie and myself, Harcourt, and then by our present President, who, before being translated to Manchester, was the Millard lecturer at Oxford. Out of thirty-two Presidents, Oxford has contributed five, Edinburgh two, Dublin one, and Cambridge also two, although without being very prophetic we can conceive that number must be added to before long.

I should have liked to speak about my associations with all the Presidents of the Chemical Society—at any rate, I should have liked to speak of the first four or five.

Richard Phillips was one of the Presidents with whom it was my good fortune to become intimately associated, and by and by he became the editor of the *Philosophical Magazine*. He was an able critic, a great conversationalist, and a newsmonger, and from his addiction to personal joking he was spoken of (independently of his position as editor) as "Phil. Mag." I was in 1851 appointed tutor at Guy's Hospital, where I was brought into association with the second President of the Society.

A word or two about myself as one of the guests on this occasion. I became Fellow in 1848, and was therefore practically one of the founders of the Society; I acted as Secretary, and filled the position of third President, in order of series, to my old tutor, Arthur Aikin. I was afterwards translated to St. Bartholomew's Hospital, and from there to the Royal Institution, where I met Faraday, of whom it is impossible to speak without regret and veneration. Then I went to Oxford, where I met Brodie. I am still attached to Oxford, and have had the advantage, the very great advantage, of having had, both before and since my appointment, a succession of assistants of whom any professor of chemistry might be proud. First was Körner, now of Milan, whose name is a household word among us, and others who have, one after the other, achieved the distinctions of being made Fellows of the Royal Society, namely Dupré, Dunstan, Hartley, Veley, and Marsh, whom, I am glad to say, is still with me. I wish to express my deep indebtedness to all of these, and to my faithful assistants, Fisher and Watts, who are with me still. I am delighted to be here among my juniors to-night, and to feel myself at home.

(To be continued).

Double Rhodanides of Divalent Copper and Cobalt with Organic Bases.—J. Calzolari.—Concentrated pyridinium rhodanide solution gives with a saturated solution of ammonium rhodanide containing copper nitrate red-brown crystals of *tris*-pyridinium cupric rhodanide, $Cu(SCN)_2.3C_5H_5N.HSCN$. *Bis*-hexamethylene tetramine cupric rhodanide, $Cu(SCN)_2.2C_6H_{12}N_4.HSCN$, may be prepared similarly, and also the corresponding cobalt salt $Co(SCN)_2.2C_6H_{12}N_4.HSCN$.—*Berichte*, xliii., No. 12.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY,

Ordinary Meeting, October 20, 1910.

Prof. HAROLD B. DIXON, M.A., Ph.D., F.R.S., President, in the Chair.

MESSRS. H. A. Tempany and J. Haycock were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Malcolm Percival Applebey, Hill View, Foxcombe, near Oxford; Manindranath Banerjee, 3, Padmanath Lane, Shambazar, Calcutta; Fred Wilkinson Barwick, Rathlyn, Kilmorey Gardens, St. Margaret's-on-Thames; Sarat Chandra Bhattacharya, M.A., Hazaribagh, Bengal, India; André Bracher, 30, Guildford Street, London, W.C.; Frederick Hugh Rochford Brady, 12, Park View Avenue, Harold's Cross, Dublin; Stewart McGregor Bosworth, B.Sc., 65, Abingdon Villas, Kensington, W.; John C. Briggs, East View, Workington; John Brown, B.Sc., Technical Institute, Timaru, New Zealand; Frederick Challenger, B.Sc., 324, Mansfield Road, Carrington, Nottingham; Reginald Thomas Colgate, 26, Birdhurst Rise, S. Croydon; Thomas Watts Coslett, Steel Road, Northfield, Worcs.; John Hughes Davies, B.Sc., Ph.D., St. Peter's College, Peterboro'; James Hugh Duncan, 18, Park Place, Cardiff; William Gidley Emmett, B.A., Caius College, Cambridge; Ainslie Jackson Ensor, B.Sc., 67, Cannon Street, Wellingborough; John George Finlayson, B.A., 13, Monarch Terrace, Blaydon-on-Tyne; George Alexander Godden, 18, Rylett Crescent, Shepherd's Bush; Edmund Knecht, M.Sc., Ph.D., Municipal School of Technology, Manchester; William Arthur Knight, M.A., 5, the Green, Marlborough; Bertram Lambert, M.A., 34, Leckford Road, Oxford; Kenneth Stewart Low, 3, Luxemburg Gardens, W.; Clement Ward Lowe, Thorneyholme, Knutsford; Malcolm McNish, Shortsands, St. Neots; James Irvine Orme Masson, M.Sc., 2, Chester Street, Edinburgh; Riko Majima, 37, Linden Gardens, Notting Hill Gate, W.; Thomas R. Merton, B.Sc., 18, Grosvenor Street, W.; Dhirendranath Mitra, B.A., 89/2, Musjeed Bari Street, Calcutta; Harold Moore, B.Sc., 84, Kalashnikeff Quay, St. Petersburg; Valliyil Govindan Nair, B.A., B.Sc., 223, Upper Brook Street, C.-on-M., Manchester; John Hamilton Paterson, M.Sc, Carmyle, Wellington Street, Grimsby; Alfred John Pennington, Oakley, Fallowfield, Manchester; Benjamin Ashwell Posford, Wood Dene, Kippington, Sevenoaks; Hari Prasad, B.A., B.Sc., 97, Roseneath Road, Urmston, Manchester; Frederick Valentine Ramsden, Alexandra Street, E. St. Kilda, Victoria, N.S.W.; Thomas John Rees, B.A., B.Sc., Cwmllynfell, Swansea Valley; Gangaram Rajendrarao Rele, 18, Entwistle Street, Manchester; Joseph Ridgway, B.A., Rownall Hall, Wetley Rocks, Stoke-on-Trent; James Beglar Robinson, Dairy School, Kilmarnock; Frederick Herbert Sharpe, The Ferns, Cressington Park, Liverpool; Percy Lancelot James Smith, M.A., Army College, Storrington, Sussex; Jwala Prasad Srivastava, B.Sc.Tech., 20, Curzon Avenue, Victoria Park, Manchester; Augustus George Terrey, 47, Cann Hall Road, Leytonstone, N.E.; Joseph Turner, Azo House, Birkby, Huddersfield; Robert Lauder Mackenzie Wallis, B.A., Llwyndu, Cardiff Road, Llanishen, S. Wales; Syed Muhammad Jusuf, B.Sc.Tech., Municipal School of Technology, Manchester.

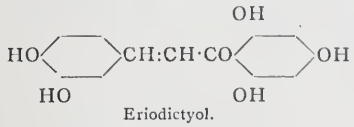
Of the following papers, those marked * were read :—

*253. "*The Constitution of Eriodictyol, of Homoeriodictyol, and of Hesperitin.*" By FRANK TUTIN.

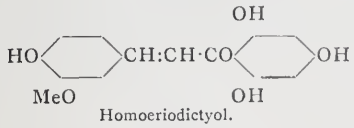
The author has methylated eriodictyol, homoeriodictyol, and hesperitin, and obtained from each of these compounds 2-hydroxy-4 : 6-dimethoxyphenyl 3 : 4-dimethoxystyryl ketone (m. p. 154°) and 2 : 4 : 6-*trimethoxyphenyl* 3 : 4-*dimethoxystyryl ketone* (m. p. 85° when air-dried,

117·5° when anhydrous), thus proving the correctness of the conclusions of Power and Tutin (*Trans.*, 1907, xci., 887) regarding the constitution of the three naturally occurring substances mentioned.

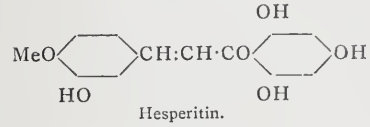
These compounds are therefore represented as follows :—



Eriodictyol.



Homoeriodictyol.



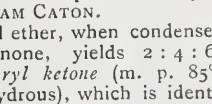
Hesperitin.

The view was expressed that naringenin is not the phloroglucinyl ester of *p*-hydroxycinnamic acid, as concluded by Will (*Ber.*, 1887, xx., 297), but 2 : 4 : 6-*trihydroxyphenyl* 4-*hydroxystyryl ketone*.

*254. "*The Synthesis of* 2 : 4 : 6-*Trimethoxyphenyl* 3 : 4-*Dimethoxystyryl Ketone, a Methyl Derivative of Eriodictyol, Homoeriodictyol, and Hesperitin.*" By Frank Tutin and Frederic William Caton.

Vanillin methyl ether, when condensed with 2 : 4 : 6-trimethoxyacetophenone, yields 2 : 4 : 6-*trimethoxyphenyl* 3 : 4-*dimethoxystyryl ketone* (m. p. 85° when air-dried, 117·5° when anhydrous), which is identical with the fully methylated product obtained from eriodictyol, homoeriodictyol, and hesperitin (compare preceding abstract).

The action of aluminium chloride and acetyl chloride on phloroglucinol trimethyl ether was shown to result in the formation of a *hydroxydiacetyldimethoxybenzene* (m. p. 127—128°) possessing the following constitution :—



*255. "*Aniline-black and Allied Compounds.*" (Part I.). By Arthur George Green and Arthur Edmund Woodhead.

The authors, after reviewing and criticising the recent work of Willstätter and Dorogi on aniline-black, gave an account of the preparation of certain intermediate substances obtained in the conversion of aniline hydrochloride into aniline-black. The first product is emeraldine, and from it four other substances have been prepared, namely, two by oxidation, nigraniline, and pernigraniline, and two by reduction, protoemeraldine and leucoemeraldine. All these compounds form a series, any member of which can be converted into any other by the use of a suitable oxidising or reducing agent. With the view of finding their molecular weight and probable constitution, these compounds have been analysed by determining the amount of hydrogen necessary to convert the more highly oxidised substances into less highly oxidised ones, and, conversely, the amount of oxygen required to oxidise the latter. From the results obtained the accompanying formulæ are assigned. (See next page).

The question as to whether the chain is open or closed is, for the present, to be regarded as unsettled.

An attempt has been made to clear up the present extremely involved nomenclature, relating to aniline-black and allied substances, and, further, it has been shown that the so-called "aniline-blacks" of Kayser, Nietzki, Willstätter, &c., consist essentially of emeraldine and nigraniline mixed with higher condensation products of at present unknown constitution.

*256. "*The Colour Changes of Methyl-orange and Methyl-red in Acid Solution.*" By Henry Thomas Tizard.

The author has measured quantitatively the changes in molecular colour of methyl-orange and methyl-red in solutions of varying concentrations of hydrogen ions.

From the results the following constants have been deduced :—

	K_a.	K_b.
Methyl-orange (at 25°) .. .. $NMe_2·C_6H_4·N:N·C_6H_4·SO_3H$	$4·25 \times 10^{-4}$	$< 10^{-14}$
Methyl-red (at 18°) .. .. .. $NMe_2·C_6H_4·N:N·C_6H_4·CO_2H$	$1·05 \times 10^{-5}$	3×10^{-13}

The value of methyl-red as an indicator was discussed, and it was shown that its "neutral-point" lies between concentrations of hydrogen ions of $10^{-5·7}$ and 10^{-7}, which are very close to one another, and to the theoretical neutral-point at 10^{-7}.

*257. "*The Hydrolysis of Aniline Salts Measured Colorimetrically.*" By Henry Thomas Tizard.

The author has applied the results of the preceding paper to the colorimetric measurement of the hydrolysis of aniline hydrochloride and acetate in aqueous solution.

A determination of the depth of colour of methyl-orange in such solutions gives directly the concentration of hydrogen ion. The method compares well in accuracy with other methods for measuring hydrolysis when the base used is weaker than ammonia, as in the salts examined; at the same time measurements can be made easily and quickly.

The results of Veley and other investigators in this field were discussed.

Discussion.

Mr. Baron asked whether the author had, in comparing the depth of colour, considered the effect of fluorescence in the indicator employed.

Mr. Tizard, in reply, said that he had not observed any fluorescence in carrying out the experiments.

258. "*The Structure of Xanthonium and Acridinium Salts.*" (Preliminary Note). By John Theodore Hewitt and Ferdinand Bernard Thole.

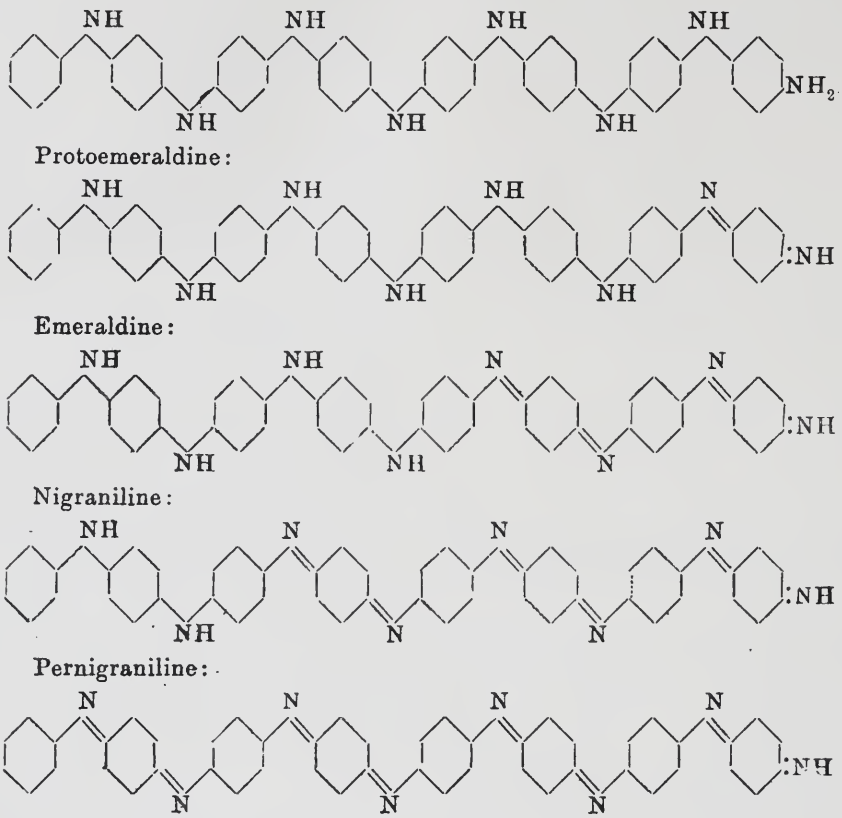
The compounds formed by xanthenol and its derivatives with mineral acids, water being eliminated, have generally been regarded as oxonium salts (Hewitt, (*Zeit. Phys. Chem.*, 1900, xxxiv., 9; Decker, *Ber.*, 1901, xxxiv., 3300). Gomberg and Cone claim that they are carbonium compounds (*Annalen*, 1909, ccclxx., 142), recognising the analogy to the acridinium compounds; the latter also receive a carbonium structure from these authors.

Kehrmann (*Annalen*, 1910, ccclxxii., 287) opposes this view, and the present authors find that whilst phenylxanthenol and phenylmethylacridol give nearly the same absorption spectra, acids effect a change in these spectra, pointing to the salts formed in the two cases having similar constitutions. Since the view that methyl iodide forms an additive product with phenylacridine of the constitution $CPh\leqslant\begin{matrix}C_6H_4I\\C_6H_4\end{matrix}\geqslant NMe$ seems untenable, the present authors agree with Kehrmann in preferring to retain an oxonium structure for the salts obtained from xanthenol and its derivatives.

Amino-derivatives of both series are under investigation.

259. "*The Application of Viscometry to the Measurement of the Rate of Reaction.*" (Preliminary Note). By Albert Ernest Dunstan.

With the object of introducing a method for the measurement of reaction velocities which will be applicable to cases where difficulties may be met with in the chemical deter-



mination of the concentrations of the reacting compounds, and will also be free from the necessity of using a substance foreign to the reaction as an indicator of the course of events, the author has studied the viscosity-time curves for many reactions, amongst which are:—(1) Moto-isomeric change; (2) isodynamic change of ethyl aceto-acetate, ethyl malonate, and acetylacetone after distillation; (3) tautomeric change of dextrose and lactose in aqueous solution; (4) hydration of aldehydes; (5) formation of thiocarbamide and carbamide from ammonium thiocyanate and ammonium cyanate respectively; (6) the benzidine transformation. In those examples where the viscosity of the end product of equilibrium mixture is sufficiently different from that of the initial compound, it is possible to calculate a velocity-constant.

260. "*Iodoacenaphthene*." By Holland Crompton and Muriel Kate Harrison.

Iodine acts on acenaphthene in the presence of yellow mercuric oxide. The acenaphthene is dissolved in boiling methyl alcohol, the solution is slightly cooled, and then a mixture of iodine (1 mol.) with rather more than the calculated amount of mercuric oxide is gradually added. The solution is finally raised to the boiling-point, and filtered. The crude iodoacenaphthene which crystallises out is first freed from mercuric iodide by dissolving it in cold chloroform, and then purified by crystallisation from methyl or ethyl alcohol. A complete purification is best effected by converting it into the picrate, crystallising this from alcohol, and then washing out the picric acid with ammonia.

Iodoacenaphthene, $C_{12}H_9I$, crystallises from alcohol in colourless needles or prisms. Fine highly refractive prismatic crystals are obtained on slow evaporation of an ethyl acetate solution. It melts at 65·5°, and decomposes at a little above 180°, with copious liberation of iodine. The *picrate* crystallises in fine orange-red needles, melting at 102·5°. It is gradually decomposed on crystallisation from alcohol. On oxidation by sodium dichromate in acetic acid solution, an iodonaphthalic acid is obtained, the anhydride of which melts at 231°. The copper salt of this acid, on heating with soda-lime, gave naphthalene and an oil which was obtained in too small an amount for identification. On fusing the acid with potassium hydroxide at 260°, 4-hydroxynaphthalic acid was obtained. From this it is probable that the acid is 4-iodonaphthalic acid derived from 4-iodoacenaphthene. It has been found, however, that whilst 4-chloro- and 4-bromo-acenaphthene form isomorphous mixtures with one another, they are not isomorphous with the iodoacenaphthene which is here described. Further experiments are therefore being undertaken to investigate the constitution of this compound.

261. "*An Improved Form of Extraction Apparatus*." By James McConnell Sanders.

The form of extraction apparatus illustrated in the accompanying diagram possesses several advantages over the usual form of Soxhlet extractor, or similar appliances in which the substance to be extracted is contained in a vertical tube the upper orifice of which is closed by the cork carrying the reflux condenser, the cork having to be removed each time a fresh quantity of material has to be introduced.

Fig. 1 shows the simpler form of apparatus, which when once mounted with its condenser is always ready for use; successive quantities of material may be introduced by simply removing the glass stopper D, the extraction being carried on with the tap A closed, when the apparatus acts as an intermittent extractor. When extraction is complete, the tap A is opened, and the solvent distilled off directly through the side-tube.

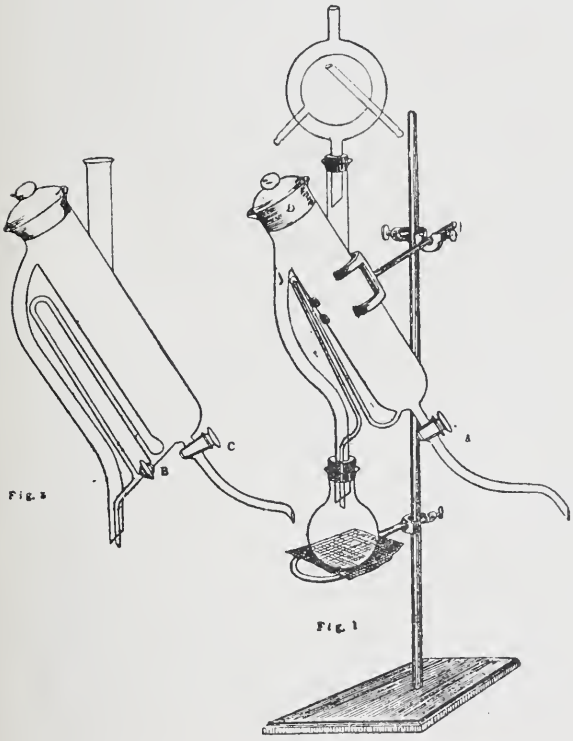
When using very volatile solvents, such as ether or carbon disulphide, the subsequent distillation of the solvent

is facilitated by removing the cartridge containing the exhausted material, and substituting a glass boiling tube containing cold water or crushed ice.

The more elaborate form shown in Fig. 2 has two taps, B and C, and when both these are kept closed the tubes *t t* act as a syphon, and the extractor works intermittently, With C closed and B open, the apparatus works as a continuous extractor, or can be used also as a reflux condenser, especially if an inner tube containing cold water or ice is used.

With B closed and C open, the apparatus can be used for distilling off the solvent, as described in the case of Fig. 1.

In the author's laboratory a large model constructed of tinned copper has been in use for several months, and has proved of great value in cases where the probable amount



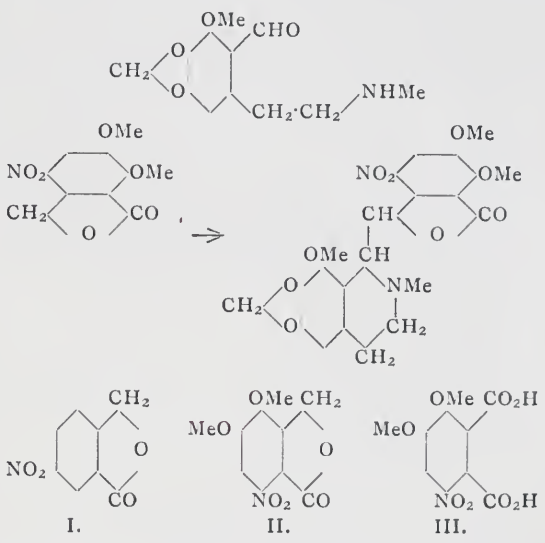
of extractive matter was unknown, since in the event of too small a quantity of material being taken in the first instance, it was an easy matter to place a succession of weighed cartridges in the extractor and extract with the same amount of solvent without dismounting the apparatus. This copper extractor has an internal capacity of 1000 cc., and in order to adapt it for use with smaller quantities of material a number of "dummy" cartridges of thin sheet copper are used to fill up a certain amount of space before placing the material in position.

262. "*The Synthesis of Nitrognoscopine and Allied Substances.*" (Preliminary Note). By Edward Hope and Robert Robinson.

The synthesis of gnoscopine (*r*-narcotine) has recently been accomplished (Perkin and Robinson, *Proc. Chem. Soc.*, xxvi., 46) by the condensation of cotarnine and meconine with the aid of potassium carbonate in alcoholic solution.

The present authors have observed that the condensation of cotarnine and nitrophthalides or their methoxy-derivatives occurs with very much greater facility.

Thus, nitrognoscopine is obtained in practically quantitative yields by boiling equimolecular quantities of cotarnine and nitromeconine in alcoholic solution for a few minutes. The reaction proceeds in accordance with the following scheme:—



The nitromeconine may be replaced by 5-nitrophthalide (I.) or by nitro-ψ-meconine (II.), the constitution of which is demonstrated by its oxidation with permanganate to the known nitrohemipinic acid (III.).

It is clear therefore that the nitro-group may be in the ortho-, meta-, or para-position in relation to the reactive ·CH_2· group of the phthalide ring.

Nitrognoscopine, $CH_2{:}O_2{:}C_{18}H_{11}O_2(OMe)_3{\cdot}NO_2$, is very sparingly soluble in boiling alcohol and the usual organic solvents, but crystallises from hot trichloroethylene in bright yellow prisms, which melt and decompose to a red liquid at 191°. It is readily decomposed by warm glacial acetic acid, yielding cotarnine and nitromeconine.

The sparingly soluble pale yellow *hydrochloride*, the *aurichloride*, and *picrate* have been prepared and analysed.

The methiodide, $CH_2{:}O_2{:}C_{18}H_{11}O_2(OMe)_3{\cdot}NO_2{,}MeI$, is a yellow crystalline powder, which melts at 205—206°.

On boiling with silver chloride in aqueous solution, the *methochloride* and silver iodide are obtained, and the addition of sodium hydroxide to the cooled and filtered solution gives a yellow amorphous precipitate of the *ammonium hydroxide*. This substance dissolves in boiling water, and the solution, on cooling, deposits orange crystals of *nitronarceine*, $C_{23}H_{26}O_{10}N_2$, melting at 160—170°, and soluble both in dilute acids and alkalis.

This decomposition is entirely similar to that by which narceine is produced from narcotine or gnoscopine.

Aminognoscopine, $CH_2{:}O_2{:}C_{18}H_{11}O_2(OMe)_3{\cdot}NH_2$, is formed by the reduction of nitrognoscopine with tin and hydrochloric acid in the cold. It crystallises from ethyl acetate in colourless lustrous prisms, melting at 205°, which are not decomposed by boiling glacial acetic acid.

Acetylaminognoscopine occurs in highly characteristic bunches of needles, melting at 198°.

Nitro-ψ-gnoscopine, prepared from cotarnine and nitro-ψ meconine, crystallises from a mixture of chloroform and alcohol in pale yellow needles melting at 184°. In general properties it resembles the isomeric nitrognoscopine.

Anhydrocotarninenitrophthalide (*nitrodesdimethoxy-gnoscopine*), $CH_2{:}O_2{:}C_{18}H_{11}O_2(OMe){\cdot}NO_2$, crystallises in prisms melting at 176–177°. It is not so readily decomposed into its constituents by means of hot glacial acetic acid as is nitrognoscopine.

Anhydrocotarnineaminophthalide,—

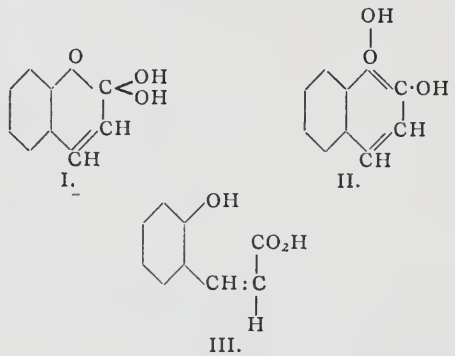
$$CH_2{:}O_2{:}C_{18}H_{11}O_2(OMe){\cdot}NH_2,$$

is prepared by reducing the nitro-compound with stannous chloride in glacial acetic acid solution. It crystallises from a mixture of chloroform and alcohol in rectangular plates melting at 216—218°.

The products of these remarkable condensations are being studied in detail, especially with a view to the elimination of the nitro-group and the consequent synthesis of some new alkaloids allied to narcotine and hydrastine.

263. "*The Constitution of Coumarinic Acid.*" By Arthur Clayton.

Two methyl ethyl ether-esters of 5-nitrocoumarinic acid have been prepared. Michael's formula (I.) for coumarinic acid is therefore incorrect. The dimethyl ether-esters of 5-nitrocoumarinic acid and 5-nitrocoumaric acid form the same bromine additive compound. Formula II. is thus excluded, and coumarinic acid is proved to be a *cis*-isomeride of *o*-coumaric acid (Formula III.).



I. II. III.

264. "*The Reduction of Chloric Acid.*" By Ralph Roscoe Enfield.

A dilute solution of chloric acid free from the presence of other acids is not reduced by sodium amalgam. A dilute solution of chloric acid may be kept in contact with methyl alcohol for several days without any reduction taking place. The velocity of reduction of chloric acid is increased by the addition of other acids. It is suggested that this stimulating effect may be due:—

1. To the mass action of the hydrogen ions in increasing the concentration of non-ionised chloric acid, on the assumption that the primary reaction is the breaking down of the non-ionised chloric acid molecule, or

2. To the purely catalytic action of the hydrogen ions, on the assumption that the reaction is an ionic one, the reduction being that of the ClO_3 ion.

The velocity of reduction of chloric acid by methyl alcohol in presence of certain concentrations of other acids was measured. Experiments were made for nitric, sulphuric, benzenesulphonic, and oxalic acids. The stimulating effects of these acids were found to be in the order of their relative strengths. The reaction between chloric acid and ferrous sulphate was examined in the same way, and the acceleration of the reaction by various acids was determined. Acceleration constants for the various acids were calculated, and shown to be in moderate agreement with the affinity constants of the acids.

These results appear to favour the view that the reduction is that of the ClO_3 ion, accelerated by the catalytic influence of hydrogen ions.

265. "*The Dynamics of the Decomposition of Persulphuric Acid and its Salts in Aqueous Solution.*" By Leila Green and Orme Masson.

The authors confirm Levi and Migliorini's work (*Gazzetta*, 1906, xxxvi., [2], 599) as to the simple unimolecular character of the decomposition in aqueous solution of sodium, potassium, and ammonium persulphates, and as to the large acceleration produced by added acids.

The decomposition of persulphuric acid differs from that of the sodium or potassium salt in being only apparently unimolecular, since its velocity-coefficient varies with the initial concentration, and is the sum of a true unimolecular constant (k_2) and a quantity proportional to this concentration (kA); also k_2 is nearly twice as large as the k_1 of the salts of the alkali metals.

The barium salt yields a curve with marked change of flexure, showing large auto-acceleration, until, when the action is half completed, all the barium has been precipitated as sulphate, and a solution of pure persulphuric acid is obtained.

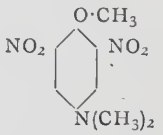
The authors suggest a theory which explains quantitatively these cases, and also those of most of the mixtures studied. Each salt has its own normal unimolecular constant which is increased by a quantity proportional to the hydrogen ions, or acid accelerator, present. The acid sulphate, which is an essential product of the action, and yet shows no catalytic effect (even although added at the outset), does not reckon in this connection as an acid, whilst added sulphuric acid counts only as a monobasic acid. Persulphuric acid has its full dibasic value.

The addition of alkalis does not alter the simple unimolecular character of the decomposition of the sodium or potassium salt, and hardly changes the value of the constant. Barium persulphate, when mixed with barium hydroxide, shows a much larger initial rate of decomposition than the pure salt, and there is also further auto-acceleration.

Most of the work was carried out at 80°. At 90° the velocities are practically ten times as great as at 70°.

266. "*Complete Methylation by Methyl Sulphate.*" By Raphael Meldola.

In the course of some experiments having for their object the preparation of compounds containing an asymmetric quinquivalent nitrogen atom combined with at least one strongly acid radicle, it became necessary to obtain, if possible, a mono-alkylated 2 : 6-dinitro-4-aminophenol (*iso*picramic acid). Some of the latter was accordingly treated with methyl sulphate and alkali in the usual way, the quantity of methyl sulphate being a little in excess of that required to introduce one methyl group. It was thought that the protective action of the nitro-groups might possibly prevent the methylation of the hydroxyl and direct the methyl group into the 4-amino-group. It was found, however, that the product was non-phenolic, and further examination showed that three methyl groups had entered the molecule, the unmethylated portion being mainly, but not entirely, unchanged *iso*picramic acid. The tendency in this case is for complete methylation to take place, the yield of trimethyl derivative being very high, in spite of the deficiency of methyl sulphate. The compound is accordingly 2 : 6-*dinitrodimethyl*-p-*anisidine*,



0·0472 gave 7 cc. N_2 (moist) at 13° and 761·7 mm. N = 17·56. $C_9H_{11}O_5N_3$ requires N = 17·43 per cent.

The substance is basic, dissolving in mineral acid to a clear solution, from which orange needles separate on neutralisation with ammonia. The melting-point of the pure compound is above 300°.

267. "*A Study of the Dissociation of the Salts of Hydroxylamine in Aqueous Solution.*" By Ernest Barrett.

The work is an outcome of the previously recorded influence of acids and alkalis on the rate of formation of acetoxime (Barrett and Lapworth, *Trans.*, 1908, xciii., 85). Aqueous solutions of hydroxylamine sulphate and hydrochloride, to which various fractions of a molecular equivalent of alkali had been added, were examined as to their electrolytic conductivity and degree of acidity, the atter colorimetrically, using *o*-nitrophenol as indicator.

Whilst the first method gave a normal result, the latter method indicated that the gradual addition of alkali to hydroxylamine hydrochloride does not produce a steady rise in the alkalinity of the solution, but that strongly marked maxima and minima occur.

268. "*The Colour and Constitution of Bromine Solutions.*" By Alfred Francis Joseph and James Nadoris Jinendradasa.

On adding a soluble bromide to aqueous bromine, the colour becomes lighter. This seems probably due to the formation of a polybromide which is lighter in colour than free bromine.

The colour of bromine water was compared with that of solutions of bromine in aqueous bromides (using potassium dichromate as an intermediate standard), and it was found that after the concentration of the bromide reached normal, further addition produced little effect on the colour. This agrees with the view that in normal bromide solution the bromine is practically wholly combined.

The colorimetric results applied to the dissociation equation $k(KBr_3) = (KBr) \times (Br_2)$ give values of k varying from 0·03 to 0·07, which are similar to those obtained by Worley in the study of the strength of solutions of equal vapour pressure. Potassium and sodium bromides and hydrobromic acid gave similar results.

269. "*The Reactivity of Ketones towards Iodine and the Relative Rates of Tautomeric Change.*" By Harry Medforth Dawson and Robert Wheatley.

The rate at which iodine reacts with various ketones in aqueous alcoholic solution has been measured in the presence of sulphuric acid as a catalyst. Dimethyl, methyl ethyl, methyl propyl, methyl butyl, methyl hexyl, phenyl methyl, diethyl, and phenyl ethyl ketones were examined. The mechanism of the change appears to be the same in all cases, and from the observed velocities with which the ketones react with iodine under comparable conditions, the relative rates at which the various ketones are converted from the ketonic to the enolic form have been obtained.

270. "*The Colour and Absorption Spectra of some Sulphur Compounds.*" By John Edward Purvis, Humphrey Owen Jones, and Hubert Sanderson Tasker.

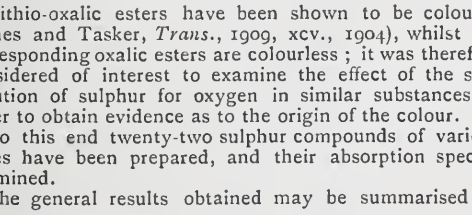
Dithio-oxalic esters have been shown to be coloured (Jones and Tasker, *Trans.*, 1909, xcv., 1904), whilst the corresponding oxalic esters are colourless ; it was therefore considered of interest to examine the effect of the substitution of sulphur for oxygen in similar substances in order to obtain evidence as to the origin of the colour.

To this end twenty-two sulphur compounds of various types have been prepared, and their absorption spectra examined.

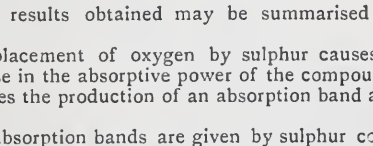
The general results obtained may be summarised as follows :—

1. The displacement of oxygen by sulphur causes a marked increase in the absorptive power of the compound, and often causes the production of an absorption band and of colour.

2. Definite absorption bands are given by sulphur compounds having the following structure, but are not exhibited by the corresponding oxygen compounds :—



I. II. III. IV.



V. VI.

Of these compounds of the types, I., II., IV., and VI. are yellow, and V. may be considered as faintly yellow in colour.

3. The group C:S must be considered a powerful chromophore.

4. In certain aromatic compounds, such as phenol and benzyl alcohol, the displacement of oxygen by sulphur results in the obliteration of absorption bands, which is probably due to the increase in general absorption.

5. Oxalyl chloride, which is itself colourless, gives yellow solutions with a number of unsaturated compounds and compounds containing oxygen or sulphur.

271. "*The Interaction of Phenyl Mercaptan and Thionyl Chloride.*" By Hubert Sanderson Tasker nd Humphrey Owen Jones.

As a result of an examination of the interaction of phenyl mercaptan and thionyl chloride (*Trans.*, 1909, xcv., 1911), the authors concluded that the change could be partly represented by the equation—

$$8C_6H_5\cdot SH + 4SOCl_2 = 8HCl + 2SO_2 + 3(C_6H_5\cdot S)_2 + (C_6H_5)_2S_4,$$

and suggested that sulphur dioxide was produced by the decomposition of sulphur suboxide (SO), which might be formed momentarily.

The evidence in support of this was as follows :—

1. The titre of the products of the interaction for alkali and for iodine was approximately that required by the above equation.

2. The liquid product of the reaction had the properties and composition of diphenyl tetrasulphide.

3. When thionyl chloride reacts with lead phenylmercaptide, $Pb(S\cdot C_6H_5)_2$, or with nickel carbonyl, sulphur dioxide is formed, and in the latter case sulphur is also produced. In both cases it would appear that sulphur dioxide has been produced by the decomposition of sulphur suboxide.

In a recent paper (*Trans.*, 1910, xcvii., 1196) Smythe and Forster criticise these conclusions, and state that there is no reason to believe that the reaction is not completely represented by Holmberg's equation (*Annalen*, 1907, ccclix., 81) :—$4RSH + SOCl_2 = R_2S_2 + R_2S_3 + H_2O + 2HCl$.

These authors have, however, entirely overlooked the evidence mentioned under 2 and 3 above, and also the fact that water was always present at the end of the reaction, and that therefore all the sulphur dioxide could not have been due to the secondary interaction between water and thionyl chloride.

272. "*Triketohydrindene Hydrate.*" By Siegfried Ruhemann.

Triketohydrindene hydrate, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C(OH)_2$ (*Trans.*, 1910, xcvii., 1438), yields with guanidine or benzamidine the compounds :—$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C(OH)\cdot NH(:NH)\cdot NH_2$ and $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C(OH)\cdot NH\cdot CPh:NH$, with hydrogen cyanide, the unstable cyanohydrin, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C(OH)\cdot CN$, and with phosphorus pentachloride, 2 : 2-dichloro-1 : 3 diketohydrindene, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CCl_2$.

The action of potassium hydroxide on triketohydrindene hydrate proceeds in three distinct phases, which are indicated by colour changes. First, a yellow coloration is formed, which is due to the production of phenylglyoxal-*o*-carboxylic acid, $CO_2H\cdot C_6H_4\cdot CO\cdot CHO$, then the solution becomes blue, and finally colourless. The colourless liquid contains the potassium salt of *o*-carboxymandelic acid, $CO_2H\cdot C_6H_4\cdot CH(OH)\cdot CO_2H$, because, with dilute sulphuric acid, it yields phthalidecarboxylic acid, $C_6H_4<\begin{matrix}CO\cdot O\\\end{matrix}>CH\cdot CO_2H$. As regards the intermediate phase of the reaction, which is characterised by the blue colour of the alkaline solution, the author puts forward an explanation based on the analogy to the similar reaction in the

case of the diketopyrrolines, when unstable blue salts are formed.

Triketohydrindene hydrate gives an intense blue coloration with α-aminoaliphatic or aliphatic aromatic acids, whereas on coloration is obtained with substituted amino-acids; for example, phenylglycine and hippuric acid, or with aromatic acids which contain the amino-group in the nucleus. So far, only two β-amino-acids have been tested, and they were found to differ, in some respects, from their isomerides, the α-amino-acids, in their behaviour towards triketohydrindene hydrate.

273. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part XVI. *The Relationship between the Chemical Constitution and the Influence of a Solvent.*" By THOMAS STEWART PATTERSON and ELIZABETH FINDLAY STEVENSON.

The relationship between the chemical constitution and the influence, on the rotation of ethyl tartrate, of various solvents were discussed.

274. "*Solubility of Calcium Phosphate in Saturated Solutions of Carbon Dioxide containing Ammonia.*" By BERNARD FOSTER and HENRY ALLEN DUGDALE NEVILLE.

The solubility of calcium phosphate, and of the phosphates in commercial phosphatic manures, was determined in saturated solutions of carbon dioxide containing ammonia. With increasing quantities of ammonia the quantity of phosphate passing into solution increases at first rapidly, and then more slowly, the solubility of phosphate then being almost directly proportional to the amount of ammonia present.

275. "*The Constitution of Sodium Aluminate Solutions.*" By ROLAND EDGAR SLADE.

Hantzsch's experiments (*Zeit. Anorg. Chem.*, 1902, xxx., 276) on the conductivity of sodium aluminate solutions have been repeated and confirmed. These experiments show that the aluminium hydroxide behaves as a monobasic acid.

The author has been unable to confirm the work of Herz (*Zeit. Anorg. Chem.*, 1900, xxv., 155) on the existence of the compound Na_3AlO_3 in solution. The work of Russ (*Zeit. Anorg. Chem.*, 1904, xli., 206) and of Wood (*Trans.*, 1908, xciii., 421) on the equilibrium between crystalline aluminium hydroxide and sodium aluminate solutions was discussed. The assumptions on which Wood calculated the acidic dissociation constant of aluminium hydroxide were shown to be far from correct.

The work of Wood (*Trans.*, 1910, xcvii., 878) on the acidic dissociation of the hydroxides of glucinum, zinc, and lead was similarly criticised.

CORRESPONDENCE.

UNIVERSITY COLLEGE NEW CHEMICAL LABORATORIES FUND.

To the Editor of the Chemical News.

SIR,—At the request of the Appeal Committee for New Chemical Laboratories, I have accepted the position of President of the Appeal Committee. It is my desire to do all that is in my power to promote the object of the Appeal. As you are aware, that object is to raise in all a sum of £70,000 for the purchase of the site in Gower Place, and for the erection thereon of New Chemical Laboratories.

It is a matter of particular urgency that the sum of £25,000 should be raised before Christmas Day in order that the Senate of the University may exercise the option to purchase the Gower Place site; towards this sum over £10,000 has now been raised. I desire to take this opportunity of presenting an Appeal not only to the many old Students of University College scattered throughout the country, but also to the many friends of University education who will realise the importance of the scheme. It will only be with the co-operation of all such persons that the remaining £15,000 will be raised in the month between to-day and Christmas Day. This is a national object, and one which demands a national response.

I shall have great pleasure in acknowledging any donations which are sent to me addressed to University College, London.—I am, Sir, yours very faithfully,

(Signed) ARTHUR,
President of the Appeal Commitee.

November 25, 1910.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Royal Society of Arts, 8. (Cantor Lecture). "Industrial Pyrometry," by C. R. Darling.
—— Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Analytical Constants of Shellac, Lac-resin, and Lac-wax," by P. Singh. "Theory of Dyeing—Resolution after Treatment with Acids, &c.," by W. P. Dreaper and A. Wilson. "Some Indian Oils and Fats," by A. K. Menon.

WEDNESDAY, 7th.—Royal Society of Arts, 8. "The Panama Canal in 1910," by V. Cornish, D.Sc.
—— Society of Public Analysts, 8. "Fischer's Modification of Volhard's Method for the Estimation of Manganese, and its Comparison with other well-known Methods," by E. Cahen and H. F. V. Little. Composition of British Wines," by E. Russell and T. R. Hodgson "New Volumetric Process for the Estimation of Tungsten," by E. Knecht and E. Hibbert. "New Volumetric Process for the Estimation of Molybdenum," by E. Knecht and F. W. Atack. "Degree of Accuracy with which the Proteins of Milk can be Estimated by the Aldehyde Method," by H. D. Richmond. "Gorgonzola Cheese," by E. Hinks. "Tests for Cocaine and certain Cocaine Substitutes," by E. H. Hankin.

THURSDAY, 8th.—Royal Society. "Colour Blindness and the Trichromatic Theory—Part II., Incomplete Red or Green Blindness," by Sir W. de W. Abney. "Sensibility of the Eye to Variations of Wavelength in the Yellow Region of the Spectrum," by Lord Rayleigh. "Trypanosome Diseases of Domestic Animals in Uganda—IV., *Trypanosoma uniforme* (sp. nov.); V., *T. nanum* (Laveran)," by Col. Sir D. Bruce and others. "Some Enumerative Studies on Malarial Fever" and "Case of Sleeping Sickness studied by Precise Enumerative Methods," by Major R. Ross and D. Thomson. "Hæmoglobin Metabolism in Malarial Fever," by G. C. E. Simpson. "Enumerative Studies on *Trypanosoma gambiense* and *Trypanosoma rhodiense* in Rats, Guinea-pigs, and Rabbits, Periodic Variations Disclosed," by Dr. H. B. Fantham and J. G. Thomson. "Life History of *Trypanosoma gambiense* and *Trypanosoma rhodiense* as seen in Rats and Guinea-pigs," by Dr. H. B. Fantham. "Experiments on the Treatment of Animals Infected with Trypanosomes by means of Atoxyl, Vaccines, Cold, X-rays, and Leucocytic Extract, Enumerative Methods Employed," by Major R. Ross and J. G. Thomson.

CHEMICAL SOCIETY RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in DECEMBER next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary of the Society, Burlington House, W., must be received on or before MONDAY, DECEMBER 5th, 1910.

The Council wish to draw attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of Research in Inorganic and Metallurgical Chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the Coal-tar and allied Industries.

GOVERNMENT GRANT for SCIENTIFIC INVESTIGATIONS.—Applications for the year 1911 must be received at the Offices of the Royal Society not later than the first day of JANUARY next, and must be made upon printed forms to be obtained from the Clerk to the Government Grant Committee, Royal Society, Burlington House, London, W.

THE CHEMICAL NEWS.

Vol. CII., No. 2663.

PILBARITE:

A New Mineral from the Pilbara Goldfields, W.A.

By EDWARD S SIMPSON, B.E., F.C.S.

The mineral described in this paper has recently been found in small quantities above the water level in the main tantalite lode on mineral lease 86 at Wodgina, Pilbara Goldfield. The geology of this district and the nature of the tantalite lode have been described by our President in *Bulletins* 23 and 40 of the Geological Survey of Western Australia. The tantalite leases are pegged out on hilly country, composed of greenstone schists, which are penetrated by numerous veins of pegmatite, these being at times sufficiently rich in tin and tantalum to constitute "lodes." The main tantalite lode is a strong pegmatite vein, whose outcrop has been traced in a north and south direction over a length of more than half a mile. Practically the whole tantalite yield of Wodgina has been obtained from this lode, or from surface fragments weathered out of it. According to Mr. Maitland's description the chief constituents of this vein are alblte and quartz. Some portions consist almost wholly of albite, other of quartz, whilst occasionally fine scaly lepidolite is a prominent mineral. Orthoclase, manganotantalite, and cassiterite have been recorded from it, and to this list must now be added pilbarite.

A few months ago a few fragments of a bright yellow ochreous mineral from this lode were sent to the author for determination. These were found to be strongly radioactive, and to contain a considerable percentage of uranium and thorium. Such minerals being of considerable interest and value at the present time, a further supply was asked for, and in response to this request a sample of about two pounds in weight was received. A very full examination of this mineral has, therefore, been possible of accomplishment. The mineral is in nodules, from the size of a pea up to that of a walnut. The largest piece weighs 30 grms., the average size of fragment being about 5 grms. The fragments are subangular in outline, and in one or two instances portions of the surface suggest crystal faces. It is evident that this mineral is a hydrous pseudomorph after a probably anhydrous parent mineral. Examination under the microscope shows that it is amorphous, and of a colloidal gelatinous or gummy texture. Such slight indications of cleavage and external crystalline form as are observed evidently owe their origin to the parent mineral, and are not inherent characteristics of pilbarite itself. The interior of the nodules are of an almost uniform bright canary yellow colour, the exterior is disguised somewhat by a brownish or reddish coating covering a thin slightly bleached zone of mineral. The chief characteristics have been determined on material from the surface of which about 2 or 3 mm. had been removed. The interior of the nodules thus prepared was found in thin slice under the microscope to be homogeneous, except for some streakiness of colour, due probably to slightly different degrees of hydration or to slight staining in places with ferric hydrate. A few minute specks of tantalite were thus seen embedded in the mineral and a little colourless mineral which appeared to be an altered felspar. The mineral is opaque, in layers thicker than one-fifth of a millimetre. Colour, canary yellow. Brittle, earthy, amorphous. Hardness, 2·5 to 3. Specific gravity, 4·4 to 4·7. Strongly radioactive. Composition, hydrated silicate of lead, uranium, and thorium. The analysis of a well scraped fragment weighing 6 grms. was :—

* Abstract of a Paper read before the Natural History and Science Society of Western Australia, August 16, 1910.

Pilbarite, Wodgina.

UO_3	27·09
ThO_2	31·34
Ce_2O_3	0·19
Y_2O_3	0·49
Al_2O_3	0·15
Fe_2O_3	0·20
PbO	17·26
CaO	0·57
MgO	0·21
MnO	trace
K_2O	0·09
Na_2O	0·04
SiO_2	12·72
P_2O_5	1·08
Ta_2O_5	0·47
H_2O+	4·16
H_2O-	3·50
He	trace
	99·56

According to Rutherford and Boltwood's value for the ratio of radium to uranium in such minerals, pilbarite would contain about 7·5 centigrms. of radium per ton; according to Mdme. Gleditsch's values probably somewhat less, being a weathered compound. In calculating a formula for pilbarite the whole of the tantalic oxide and the requisite amount of manganese and iron oxides to form tantalite are rejected, there being abundant evidence in support of this. The traces of alumina and alkalis are also neglected as being certainly present as inclusions of mica or felspar. The phosphoric oxide is probably present as monazite or xenotime. The formula, with these allowances, is $PbO.UO_3.ThO_2.2SiO_2.2H_2O+2H_2O$. The only two minerals with a formula approaching pilbarite are thorogummite and Meckintoshite. Both of these minerals crystallise in the tetragonal system. It is evident that in the presence of lead oxide as an important constituent and also in the relative proportions of uranium oxide, thoria, silica, and water, pilbarite differs essentially from these minerals. In crystalline form it also differs essentially, and one is therefore justified in considering it a new species.

Pilbarite dissolves readily in strong or slightly diluted hydrochloric acid, leaving a flocculent residue of silica. It is completely decomposed by nitric and sulphuric acid, either concentrated or moderately dilute, but with these acids in addition to silica a bulky mass of difficultly soluble thorium and lead salts separates out. During decomposition with hydrochloric acid a fair number of gas bubbles were seen to be given off, which were at first taken to be carbonic acid, but in view of the possibility of helium being present as the result of degradation of uranium, special efforts were made to collect the gas free from air or other gaseous impurities and to examine it. The apparatus used was simply made, but quite effective for the measurement of the helium to one-fiftieth of a cubic centimetre. The helium was determined in both uncrushed and finely crushed mineral. Since Moss has shown that helium escapes on grinding a radio-active mineral, and since the generally accepted theory is that helium is only mechanically imprisoned in the mineral, it was to be expected that more helium would be obtained from the uncrushed than from the crushed mineral. The actual results obtained were :—Helium per grm. of mineral, crushed mineral, 0·22, 0·26 cc.; uncrushed, 0·38, 0·39 cc. Sulphuric acid was found to be the best for the liberation of helium from the powdered mineral, hydrochloric being so rapid in action that the apparatus could not be filled and stoppered without loss of gas. In the case of the uncrushed mineral, which was in masses of about 0·5 grm. each, sulphuric acid was found to be useless, as it failed even after two days to penetrate to the centre of the mineral, which became protected by a coating of insoluble sulphate of lead and thorium. Hydrochloric acid of 5E strength, on the con-

trary, was found to be conveniently slow in action in the cold, and very energetic on heating, lead, uranium, and thorium rapidly dissolving and leaving a flocculent mass of silica. The greater part of the helium was obtained in this way in half-an-hour, the whole of it at the end of about eight hours. As to the nature of the gas evolved, it was found to suffer no diminution in volume when agitated with caustic potash solution or with alkaline pyrogallate. It was not therefore either carbon dioxide or oxygen. With the kind assistance of Mr. J. B. Allen an attempt was made to prepare a spectrum tube of the gas, but in the absence of suitable tubes all our efforts resulted in failure. Whilst positive evidence of identity is lacking, there can be no doubt that the gas was wholly or almost wholly helium, a gas given off in greater or less quantity from all radio-active minerals when suitable means are taken to release it.

The greatest interest attaches to the accurate determination of the helium in radio-active minerals, since recent researches, particularly those of Rutherford and Strutt, have indicated that helium may by its slow accumulation, be acting as a chronometer of geologic time. Working on the mineral zircon from lava of known ages, Strutt showed that the ratio of helium in cubic centimetres to uranium oxide in grms. was a function of the age of the mineral. In calculating this ratio thoria is reckoned as equivalent in helium production to one-fifth its weight of uranium oxide. This ratio was found to be less than unity for rocks of Tertiary age, between 10 and 30 for rocks of Palæozoic age, and over 50 in the case of a single rock of Archæan age. The "helium ratio" for this pilbarite is 2·9, which would indicate that this mineral was evolved from its parent in post-palæozoic times, if all previously accumulated helium be assumed to have been liberated during the hydration and possible oxidation which then took place. Working on the principles outlined above, an attempt to estimate the age of the mineral resulted in it being placed at thirteen million years. At least two counterbalancing effects vitiate the above result to an unknown amount. These are the leakage of helium from the mineral before its estimation, and secondly the unknown amount of helium generated by the parent mineral and retained by pilbarite at the outset of its existence as such.

It is evident from what has been said that pilbarite is strongly radio-active. To test this photographically a special rapid plate was covered by a sheet of black glazed paper, which was again covered by a mask of lead-foil pierced by a pattern. Over the lead-foil was a sheet of thin tissue paper, and on that a heap of powdered pilbarite was placed. After forty-eight hours the plate was developed, and a strong radiograph obtained of the perforations in the lead. An appreciable amount of radiation had also passed through the lead-foil, which was only 0·13 mm. in thickness, the outlines of the heap of powdered mineral being clearly discernible. A freshly scraped fragment of pilbarite placed in a Glews scintilloscope yields a rapid succession of flashes due to the emission of alpha rays, *i.e.*, to the impact of electrically charged atoms of helium on the screen of zinc sulphide. Heated in a closed or open tube, pilbarite gives off much water and darkens somewhat in colour. Before the blowpipe on charcoal it is infusible and turns black. If some of the powdered mineral be heated with sodium carbonate on charcoal, a black slag is formed in which small globules of metallic lead can be seen. A fragment heated in a microcosmic salt bead gives the reactions of uranium, an unaffected residue of silica and thoria remaining.

A search was made for evidences of radio-activity in the hornblende schists enclosing the lode in which pilbarite occurs. When a small crystal of even a moderately radio-active mineral (such as radium-bearing varieties of zircon, apatite, or allanite) is enclosed in hornblende, biotite, or other similar mineral, the effect of the active rays on the enclosing mineral can be clearly perceived under the microscope. For a distance of about one-twenty-fifth of a millimetre in every direction from the surface of the active mineral the enclosing hornblende is discoloured, and this discoloured portion of the matrix is usually more strongly pleochroic than the unaffected portion. Such pleochroic halos, as they are called, are spheroidal or ellipsoidal, according to the shape of the crystal of zircon, &c., which gives rise to them. It is interesting to note that they were found to be abundant in the hornblende of the Wodgina schists. The phenomenon is, of course, known in many other parts of the globe, particularly, so far as this State is concerned, in rocks from Kalgoorlie, Ravensthorpe, and the Darling Ranges.

At the conclusion of his lecture Mr. Simpson exhibited under the microscope several specimens of the new mineral and the surrounding rocks.

REPORT ON GASEOUS COMBUSTION.*

By WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S.

(Continued from p. 262).

SECTION III.—*The Pressures produced by Gaseous Explosions.*

MANY investigators, from the time of Bunsen's well-known experiments in 1867 onwards, have measured the pressures produced in gaseous explosions, with doubtless considerable success so far as what may be termed the mean effective pressures are concerned. As the subject is at present engaging the attention of a Committee appointed by the Association in 1907 any lengthy reference to it in this report may seem superfluous. Nevertheless, if only for the sake of completeness, a brief *résumé* of our present knowledge may not be out of place. The explosion vessel employed by Bunsen was a stout glass tube 8·15 cm. long, 1·7 cm. internal diameter, and of 18 cc. capacity. It was closed by a suitable valve, the load on which could be adjusted until it was just lifted when the explosive mixture was fired by means of a powerful spark passed along the axis of the tube. Bunsen considered that the combustion would occur under adiabatic and "constant volume" conditions, and he identified the rate of ignition of a particular mixture with that of the completion of chemical change. In calculating from his results the corresponding flame temperatures he assumed the constancy of the specific heats of steam and carbon dioxide. Finding that the pressures recorded in the cases of electrolytic gas and of a mixture of carbon monoxide and oxygen in their combining proportions (namely, 9·5 and 10·1 atmospheres respectively) were somewhat less than one-half of those theoretically required on the above assumptions, he concluded that in each case combustion had proceeded *per saltum*, owing to the supposed theoretical flame temperatures exceeding the limits at which steam and carbon dioxide respectively are completely dissociated. The problem was again attacked independently by Mallard and Le Chatelier in 1883 (*Annales des Mines*, Sec. 8, vol. iv.), and by Berthelot and Vieille in 1885 (*Ann. Chim. Phys.*, [6], iv., 13). The last-named fired various gaseous mixtures at atmospheric pressure in a spherical iron bomb, measuring the effective pressures by the movement of a light piston working against a spring in a tube attached to the bomb. In order to gain some information respecting the possible cooling influence of the walls upon the effective pressures recorded, three bombs of different capacities—namely, A, of 300 cc.; B, of 1500 cc.; and C, of 4000 cc.—were employed. The results, expressed in each case as atmospheres in excess of the atmospheric pressure, are given in the accompanying table. (See next column).

Perhaps the most notable feature about these results is the smallness of the difference between the pressures observed with bombs A and C in any particular case. These differences might at first sight be attributed to the (sup-

* Read before the British Association (Section B), Sheffield Meeting, 1910.

	Bomb A.	Bomb B.	Bomb C.
Capacity, in cm.^{3}	300	1500	4000
Surface, in cm.^{2}	216	648	1220
Surface per unit volume	0·72	0·43	0·33
Diameter, in cm.	6·0	14·2	21·7
Length of firing piece, in cm.	6·3	5·3	6·3
Travel of flame before reaching the piston, in cm.	9·1	16·3	24·8

Mixture exploded.	Pressure, in atmospheres.		
$2H_2 + O_2$	7·41	9·69	9·80
$2CO + O_2$	9·29	9·93	10·21
$CH_4 + 2O_2$	13·9+	14·81	16·31
$C_2N_2 + O_2$	—	—	25·11
$C_2N_2 + 2O_2$	—	—	20·96

Mixture.	Time required for flame to travel from the firing piece to piston of indicator, in seconds.		
$2H_2 \cdot O_2$	0·00104	—	0·00214
$2CO + O_2$	0·01286	—	0·01551

posed) much smaller cooling influence of the walls of the bomb C as compared with bomb A, but if this were the true explanation the difference should be greater with the slow-burning $2CO + O_2$ mixture than with the fast-burning $2H_2 + O_2$, whereas the opposite was the case. Moreover the fact that dilution of the mixture $2H_2 + O_2$ with twice its own volume of nitrogen almost obliterated the difference between the pressures observed in the cases of bombs A and C (the ratio pC/pA for the diluted being 0·95, as against 0·76 for the undiluted mixture) is all against the cooling theory. The more probable explanation is to be found in the fact that, owing to the much longer travel of the flame before it reached the piston of the indicator in bomb C as compared with A, the explosion would be in a more advanced phase of its development, and this would be most marked in the case of the fastest burning mixtures. Berthelot and Vieille assumed that in the above experiments completion of the combustion synchronised with the attainment of maximum pressure, and attributed the marked disparity between the observed pressures (bomb C) and those calculated from the heats of combustion (on the assumption of adiabatic conditions) to a rapid increase in the specific heats of steam and carbon dioxide at high temperatures. They considered it improbable that dissociation phenomena play any conspicuous part in limiting the pressures attained.

Mallard and Le Chatelier (*loc. cit.*), who used a Bourdon gauge for measuring pressures and applied a "cooling correction" to their results, arrived at practically the same conclusion as Berthelot and Vieille (*Ann. Chim. Phys.*, [6], iv., 13) respecting both the increase of the specific heats of steam and carbon dioxide with temperature and the small if not negligible influence of dissociation. They calculated that the temperature of the flame when moist electrolytic gas is exploded in a closed vessel at atmospheric pressure is about 3·350°, and that the mean molecular heat of steam at constant volume between 0° and 3350° is 16·6. In the case of the mixture $2CO + O_2$ they concluded that the molecular heat (C_d) of carbon dioxide rises to 13·6 at 2000°, above which temperature dissociation comes into play.

The experience of all subsequent investigators has confirmed that of Bunsen and the French savants, in so far as the facts of the case are concerned. It may be taken as commonly agreed that the maximum effective pressures recorded when gaseous mixtures are fired in closed vessels are always considerably less than those calculated on the assumption that the whole heat of combustion is communicated without loss to the products, and that the specific heats of the products do not vary with temperature. Thus in the case of Mr. Dugald Clerk's experiments, where hydrogen and air mixtures were exploded at atmospheric pressure in a closed cylindrical vessel 21 cm. long, 17·75 cm. diameter, and 5·2 litres capacity, the maximum pressures, recorded by a Richard's indicator making a graph on a revolving drum, varied between about 50 and 60 per cent of those calculated on the above assumptions, as follows :—

Mr. Dugald Clerk's Experiments (1884-85).

	Vols air to 1 vol. hydrogen.		
	2½.	4.	6.
Maximum pressure found (atmospheres)	6·44	5·63	3·80
Maximum pressure calculated on the above assumptions (atmospheres)	13·0	9·45	7·0

Another feature (since confirmed by many subsequent observers) brought out by Mr. Clerk's experiments was the very short time required for the attainment of maximum pressure relative to the subsequent cooling period. Thus in the case of the mixture of 1 vol. hydrogen with 4 vols. air, the maximum pressure of 68 lbs. per square inch above the atmospheric was attained in 0·026 sec., whereas the subsequent cooling period occupied 1·05 sec., or forty times as long.

The great disparity between the found and "calculated" maximum pressures has been attributed by the various investigators concerned to one or other of the following causes, namely : —

1. *To the marked increase in the specific heats of steam and carbon dioxide with temperature.* That this is a true cause is now generally admitted ; as, however, the subject was fully dealt with in the first report of the Committee appointed by the Association in 1907 for the investigation of gaseous explosions, it need not be considered in any detail here.

2. *To the fact that in ordinary gaseous explosions, where detonation has not been determined, combustion is by no means instantaneous, and may not be completed within the period required for the attainment of maximum pressure.* Mr. Dugald Clerk put forward this suggestion as long ago as 1886 (*Proc. Inst. Civil Engineers*, 85) in criticising the conclusions of Mallard and Le Chatelier respecting the great increase in the specific heats of steam and of carbon dioxide with temperature. He considered it highly probable that combustion extends far into the actual "cooling period" in gaseous explosions (and hence the long drawn out "cooling curve"), so that the system loses a certain part of the heat of combustion before the chemical action is completed. This idea of a continued combustion finds support in H. B. Dixon's photographic researches, and chemists generally will concede its reality in any gaseous combination in which detonation is not determined. But to what extent it may be held to affect the pressures actually recorded by explosions is still a matter of conjecture.

3. *To loss of energy by direct radiation.* Thus in the explosion of a mixture of hydrogen and oxygen it is conceivable that the *initial* action results in the formation of an intensely vibrating molecular complex from which steam issues as the first recognisable product. Some experiments made in 1890 by Robert von Helmholtz (*Beiblätter*, xiv., 589) showed that non-luminous hydrocarbon flames radiate about 5 per cent of the heat of combustion of the gas, and more recent experiments by Prof. Callendar and Mr. Nelson show that the heat radiated from an ordinary non-luminous Bunsen flame may amount to between 15 and 20 per cent of the total heat of combustion, a figure which is in close agreement with the results of experiments carried out by Mr. E. W. Smith under the auspices of the Gas-Heating Research Committee appointed by the Institution of Gas Engineers in conjunction with the University of Leeds (see pp. 10—13 of the Committee's Second Report, 1910). There is, therefore, little doubt but that this cause is truly operative in gaseous explosions.

4. *To dissociation of products* (steam and carbon dioxide).

In the case of two combining gases producing a dissociable product, it is clear that if the average temperature in the system reaches that at which dissociation begins the combustion must be delayed whilst heat escapes from the system by radiation and conduction. Qualitatively the partial dissociation of steam and carbon dioxide has been proved at temperatures which are certainly exceeded by those of explosion flames, but it may be urged that, inasmuch as all experiments upon dissociation have up to the present involved contact with hot solid surfaces, there is no positive evidence that the phenomenon would play any conspicuous part in an unconfined gaseous system. On the other hand, there is direct experimental evidence of the attainment of enormously high temperatures in the explosion wave, temperatures which would generally be considered as far beyond that of the initial, or perhaps even of the complete, dissociation of steam or of carbon dioxide. Moreover, the fact that the rate of explosion of electrolytic gas is retarded rather more by an excess of oxygen than by a corresponding excess of nitrogen is inconsistent with the supposition of any appreciable dissociation of steam in the explosion wave, and photographic records give no evidence of continued combination in the rear of the wave except where there are two or more chemical stages in the combustion.

(To be continued).

BANQUET TO PAST-PRESIDENTS OF THE CHEMICAL SOCIETY.

November 11, 1910.

(Concluded from p. 276).

Sir Edward Thorpe in proposing the toast of "The Foreign Members," said:—

It is a saying no less true than trite that "Science knows no geographical limitations." She recognises no national frontiers. Science is as much the common property and heritage of mankind as is the all pervading air we breathe and which we all alike share. No nation or people has any exclusive property in science, any more than it has in the universal ether or in the forces of nature. This fact is recognised in the almost universal practice of scientific societies to welcome within their ranks workers in science of every nationality. The men of science constitute one large brotherhood; they may speak a variety of tongues; they may owe allegiance to many rulers, but they are all engaged in a common cause, and they work and strive together in honourable rivalry with a unity of aim, and that is to discover and elucidate scientific truth, and to apply the knowledge of that truth to the amelioration of our common humanity. We Britishers are proverbially a sporting people. We truly love a race of any kind; competition and the struggle for supremacy are as breath to our nostrils. It is a national characteristic and pervades every department of our national activity. But your true sportsman recognises and acclaims merit wherever he meets with it. If he wins, he wears his laurels modestly; if he loses, he takes his beating manfully, and offers his congratulations to the better man. I believe we carry this characteristic into the grand international struggle in which, as men of science, we are engaged. The good will which the Chemical Society bears to its foreign colleagues is reflected in the long list of its honorary and foreign members. From the earliest days of its inception, the Society has extended the hand of good fellowship to our foreign colleagues, and we are proud that we number some of the most eminent of them among our Fellows. We believe they appreciate the spirit in which our invitation has been extended to them. We, in our turn, are grateful to them for the honour and the distinction they have conferred upon us. It is with a feeling of deep gratitude that I invite you to drink to their health, and that I ask you to allow me to associate with the toast the names of Professor Haller and Professor Wallach. These gentlemen, the one President of the Chemical Society of France, the other President of the Chemical Society of Germany, are charged with messages of felicitation to the veterans whom we are assembled here to honour. On this account you will extend them your warmest greeting. You will recognise that each of them represents a nation which has played a long and honourable part in the science to which we are all attached, and which it is our privilege to serve.

Professor Albin Haller—L'hommage que vous rendez ce soir à vos jubilaires procède, toutes proportions gardées, du même sentiment que celui très touchant, que vous avez rendu au cours de cet été, au noble souverain qui a présidé aux destinées de l'empire avec tant de tact, tant d'autorité et tant de bonheur.

Ce sentiment est fait d'affectueuse déférence et de sincère gratitude envers les hommes qui, à des titres divers, et quelles que soient leurs conditions sociales, ont honoré l'humanité et ont jeté quelque éclat sur votre pays.

De même que la France s'est associée sincèrement et de tout son cœur à votre deuil national, de même la Société chimique de Paris a tenu à apporter aux savants vénérés, dont vous célébrez aujourd'hui la brillante carrière, un témoignage de profonde sympathie et de cordiale reconnaissance pour les services qu'ils ont rendus à la science et à leur patrie.

L'estime que vous m'avez témoignée, en me conférant le titre tant envié de Membre honoraire de votre Société, me vaut, en ce jour, la joie très douce d'assister à cette réunion et de pouvoir vous exprimer la satisfaction que j'éprouve d'être l'interprète de tous nos collègues de France envers les héros de cette fête.

La première en date, de toutes les sociétés de Chimie qui existent de par le monde, votre Société a servi de modèle à toutes celles qui sont écloses à sa suite.

Son développement est intimement lié à l'évolution de la Chimie même pendant la seconde moitié du siècle dernier, et son influence, sa prospérité, sont dues autant aux hommes marquants et dévoués qui l'ont présidée qu'aux nobles et fortes traditions qu'ils ont instaurées.

Comme vos aînés vous vous êtes toujours attachés à confier sa direction aux plus vaillants et aux plus qualifiés de vos émules.

En toute circonstance, à toute époque, vous ne manquez pas de vous inspirer de votre noble adage:—

"The right man in the right place."

Il serait téméraire de vouloir énumérer, après votre très honorable Président, M. le Professeur Dixon, tout ce que la science doit au dévouement, à l'esprit d'invention et à l'habileté expérimentale des maîtres sympathiques auxquels vous rendez hommage ce soir.

Tous, en leur temps, ont tracé plus ou moins profondément leur sillon et ont donné l'exemple d'un labeur fécond et désintéressé, tout en assurant la prospérité de votre Société.

Tous les cinq ont marqué lec multiples incursions qu'ils ont faites dans le domaine de la science, par des découvertes inattendues, des observations ingénieuses et des aperçus pleins de hardiesse et d'originalité.

Sans doute, l'apport constant de clartés et de faits nouveaux a souvent pour effet de dissimuler sous le voile de l'anonymat les vérités établies par nos devanciers, tant elles paraissent simples et évidentes aux esprits superficiels. Elles n'en font pas moins partie de notre patrimoine intellectuel et le nom de leurs auteurs restant à jamais gravé dans les Annales de la Science, apparaîtra au grand jour chaque fois qu'il se trouvera un chercheur désireux de remonter à l'origine de nos connaissances et d'en faire l'inventaire.

A l'heure présente, les noms de M. le Professeur Odling, de Sir Henry Roscoe, de Sir William Crookes, du Dr. Hugo Muller, et du Dr. A. G. Vernon Harcourt éveillent en nous un sentiment de vive reconnaissance pour l'œuvre originale et savante dont ils ont doté la science et pour le bel exemple de labeur qu'ils nous ont donné.

En sa qualité de fille aînée de votre Compagnie, la Société Chimique de France m'a chargé de traduire les sentiments de haute estime et de respectueuse sympathie qu'elle éprouve envers les cinq Jubilaires en leur décernant à chacun sa médaille à l'effigie de notre grand Lavoisier.

A l'hommage qu'elle rend ainsi à leur profond savoir, s'ajoutent ses vœux les plus ardents et les plus sinceres pour qu'ils contribuent pendant de longues années encore au progrès de votre Société et à la notoriété scientifique de la nation britannique.

Professor Dr. Otto Wallach—I wish to tender my most sincere and hearty thanks for the kindly feeling which has prompted my invitation for this auspicious occasion, and also for the friendly sentiments which have been expressed towards the foreign members of this Society.

At the present time it is not easy for a German professor to leave his work in order to undertake a long journey. I should, however, have been extremely sorry to miss the opportunity of personally stating how highly I prize my honorary membership of the Chemical Society.

Much less would I, as a member of the sister German Society, desire to refrain from conveying to the Past Presidents of the Chemical Society an expression of the veneration and esteem in which they are held by German chemists.

If I may be permitted to add a few words more, I will ask to be allowed to speak in my own language. You will probably understand my German better than my English, and I also believe that what one desires to say can better be expressed in one's mother tongue.

Wenn wir, sehr geehrte Herrn, uns zu vergegentwärtigen suchen, welche Chemiker früher in England die Entwickelung unserer Wissenschaft in besonderer Weise gefördert haben, so werden wir in Erstaunen gesetzt eine wie grosse Anzahl von Persönlichkeiten daran betheiligt war. Vor unserem geistigen Auge ziehen da ausgezeichnete Männer wie ein glänzender Triumphzug vorüber, der mit den ersten Anfänge der Chemie beginnt und sich bis zum heutigen Tage erstreckt.

An der Spitze dieses imposanten Zuges schreitet die grosse Forchergestalt *Robert Boyle's*. Ihm folgen andere Koryphäen der Wissenschaft in ununterbrochener Kette. Als in den meisten heutigen Kulturländern "Chemie" noch ein unbekannter Begriff war, entdeckte *Priestley* den Sauerstoff und lehrte zugleich als erster, wie man überhaupt mit Gasen operieren muss. Mit den Gasen, von denen man früher manche für nicht coërcibel hielt, die man jetzt nach den wundervollen Methoden von Prof. *Dewar* leicht in flüssigen Zustand zwingt. Welche unerwartete Erweiterung and Weiterentwickelung die Kenntniss der Luftarten in unseren Tagen durch die ewig denkwürdigen Untersuchungen von *Lord Rayleigh* und *Sir W. Ramsay* erfahren hat, bedarf keines Hinweises. Betrachten wir weiter die Entfaltung unseres Zuges, so sehen wir nach Priestley *Cavendish* erscheinen und vor allen ragt *Dalton* hervor, mit der Atomtheorie die Basis für die theoretische Chemie schuf. Mit Dalton kommt *Humphry Davy*. Wenn wir heut das halbhundertjährige Fellow-Jubiläum unseres Past Presidents feiern, so dürfen wir dabei wohl der Thatsache gedenken, dass in diese Tage auch ein Centenar-Jubiläum fällt. Denn grade 100 Jahr sind es, dass—im November, 1810—H. Davy vor der Royal Society jene berühmte Abhandlung verlas, in der er die elementare Natur des Chlor aussprach. Wenige Jahre vorher hatte er die Welt durch Entdeckung der Alkali-metalle in Staunen gesetzt. Aber Davy hat jener Zeit noch etwas anderes entdeckt, wofür ihm die wissenschaftlische Welt dankt: er hat das Talent *M. Faraday's* endeckt und der Chemie zugeführt.

Die Anwendung der Faraday'schen electrolytischen Gesetze gehört heut zu unserem unentbehrlichsten chemischen Handwerkszeug. Neben diesen und vielen anderen, fand Faraday bekanntlich auch das Benzol auf, die Muttersubstanz des Anilins, aus dem der verehrungswürdige *W. H. Perkin*, sen., dem wir—ebenso wie seinen Söhnen—so viele wichtige Arbeiten auf dem Gebiet der organischen Chemie verdanken, den ersten technisch brauchbaren Anilinfarbstoff herstellte.

Bei Erwähnung des Benzols gedenken wir weiter *Couper's*, der sich mit *Kekulé* in den Ruhm theilt, die Idee der Atomverkettung concipiert zu haben. Die Nennung von Kekulé's Namen bringt uns wiederum in die Erinnerung, dass Kekulé hier in London Assistent von *Stenhouse* war. Kekulé hat, wie so viele deutsche Chemiker mit, vor und nach ihm—wie die *A. W. Hofmann*, *Schorlemmer*, *Dittmar*, u. a.—in diesem gastlichsten Land der Welt auch Gastfreundschaft genossen. Den Dank den wir England dafür schulden wird man in Deutschland immer lebendig finden. Wie könnte ich in dieser kurzen Stunde sie nun aber weiter alle hier aufzählen, die Träger klangvoller Namen, die *Graham*, *Williamson*, *Frankland* u. a. die wir in dem Theil des Triumphzuges englischer Wissenschaft finden, der an vergangene Zeiten mahnt! Der Blick in die Vergangenheit erweckt sonst leicht das Gefühl der Trauer, über das, was wir nicht mehr besitzen. Aber davor sind wir heut geschützt. Denn wir haben die grosse Freude und das grosse Glück in den Männern, die zu feiern wir zusammengekommen sind, Repräsentanten einer der glänzendsten älteren Epoche der Chemie noch frisch und lebenskräftig unter uns zu wissen und ihnen den Dank dafür darbringen zu können, dass sie durch ihre Arbeit eine Saat ausgestreut haben, deren reife Frucht die junge Generation der Chemiker heut erndtet.

War es doch Prof. *William Odling*, der bedeutsamen Antheil an der Ausgestaltung der Typentheorie genommen hat. Er hat ferner schon 1857 von dem "Ersetzungswerth" von Wasserstoff und Sauerstoff gesprochen und die Werthigkeitstheorie vorbereitet.

Sir *Henry Roscoe*, dessen Arbeiten über die Isolierung und über die Eigenschaften des Vanadium's für immer ein Vorbild exacter chemischer Forschung bleiben werden, hat in seinen mit R. Bunsen gemeinsam ausgeführten photochemischen Untersuchungen die Grundlage für die heutige Photochemie mit geschaffen.

Sir *William Crookes* hat nicht nur durch Entdeckung des Thalltum's die Chemie bereichert. Seinem genialen Forscherblick offenbarte sich zuerst die "strahlende Materie," deren Erscheinung in der modernen Physik eine so hervorragende Rolle spielt.

Wenn, weiter, heut die katalytischen Erscheinungen wieder ganz besonders in den Vordergrund des chemischen Interesses gerückt sind, so geziemt es sich der Thatsache zu gedenken, dass Dr. *Hugo Müller* 1862 die katalytische Wirkung des Jod's bei Halogenisierungs - Processen aufgefunden hat.

Die Verdienste Dr. *Vernon Harcourt's* um die analytische und angewandte Chemie sind in England bekannt.

Wir sehen: die hochverehrten Past Presidents sind nicht nur Leiter der Chemical Society gewesen, sondern auch Leiter auf den Pfaden der Wissenschaft. Damit haben sie Schule gemacht und daher bis zur heutigen Stunde nach beiden Richtungen hin stets würdige Nachfolger gefunden. Die Chemical Society hat unter ihren trefflichen Praesidenten in der Chemischen Welt immer wachsende Bedeutung gewonnen und mit Bewunderung und Hochactunge blicken die auswärtigen Fachgenossen auf die von ihr ausgehenden Leistungen.

Dieser hochgeschätzten und angesehenen Gesallschaft in der sich die wissenschaftlich chemischen Kräfte Englands zusammengeschlossen haben, bringe ich, zugleich im Namen der *Deutschen Chemischen Gesellschaft*, die herzlichsten Wünsche für ihr Gedeihen und ihre glückliche Weiterentwickelung bis in eine ferne Zukunft!

Sir William A. Tilden, in proposing the toast of "The Guests," said—The object of this gathering is to offer to our senior Past Presidents an expression of affectionate homage. On such an occasion we desire before all things the sympathy of our friends. I rise, therefore, with great pleasure, to ask you to return thanks to the large number of eminent men who have assembled with us to-night, and who, by their presence and by the words which have been expressed by some of them, have

added lustre and fervour to the occasion. Among them are, not only representatives of science, but of a great variety of other interests, and this is a proof that our senior Past Presidents are known and honoured far beyond the circle which is represented by the Chemical Society. I will only venture to mention the names of a few of our guests, and the toast which I have the pleasure to propose will be coupled with three of them. We have with us a member of the Government, and we are glad to be honoured by his presence; the House of Commons is strongly represented by half a dozen eminent members. Then there are the President and the Secretaries of the Royal Society, who are never missing on any occasion when honour is to be given to the votaries of science, and we have the President and Treasurer of the famous Royal Institution, the home of chemistry from Davy to Dewar. To the Presidents of the French and German Chemical Societies we owe a very special expression of thanks, not only for their kind and sympathetic words, but for the immense trouble they have taken in making long journeys for the express purpose of attending to-night. The Presidents of a number of kindred societies which work on similar lines to the Chemical Society are also present as well as representatives of other institutions, educational, scientific, and so forth. Among these representatives I hope you will excuse me if I refer specially to the venerable Chancellor of the University of Aberdeen. Beside these, we have a number of gentlemen representing not only science, but literature, while a very eminent sculptor sits not far from me. I give you the toast of "The Guests," coupled with the names of his Grace the Duke of Northumberland, who is expected to become a member of the Council of the Royal Society, Mr. Herbert Samuel, Postmaster-General, and Herr Eyde, who represents what may be called the Chemical industry of the future.

The DUKE OF NORTHUMBERLAND.—We have felt it a very great honour to be the guests of yourselves upon this occasion, and to have had the privilege of joining in honouring the distinguished Past Presidents whom you have honoured to-night. I should like to say a word or two to express my admiration of, and gratitude to, Sir William Crookes. We all know that he has gone through many arduous struggles, and we know that he has made a reputation for manipulation, for patience, and research. I venture to think no finer manipulation has been displayed by him or greater patience than that of piloting the President of the Royal Institution through his duties. I am struck by the great advances in civilisation which are depicted by the menu. I see on the outside a very fine picture, the portraits of five Past Presidents of this Society; but I observe there is a sixth who occupies a very large space in the page, and I have no doubt it is a very distinguished Past President of the Chemical Society. I can only say that if I had had to dine with him I should have brought with me hard-boiled eggs! If one looks at the menu, he will see that chemistry is devoted to a very different object from which it is supposed to be. Some gentlemen might perhaps inform us what chemical action is going on now. I thank you on behalf of the guests.

The Right Hon. HERBERT SAMUEL, M.P.—At this hour I shall earn your gratitude if I suppress the speech I should otherwise have delivered—incisive, eloquent, brilliant, humorous, and perhaps lengthy, as you may assume it would otherwise have been. I wish to join in expressing the gratitude of the guests for the invitation that has been tendered to us. It has been a privilege to us all to join in doing honour to men whose lives have been finely spent, men who have pursued research for its own sake. They have "set their hearts upon the goal, not on the prize," and have added fresh lustre upon the annals of British science.

Herr GENERALDIREKTOR S. EYDE.—So many eminent speeches have been made here to-night that were it not for the fact that I have been called upon to speak, I should never have ventured to do so.

Having, however, been afforded this opportunity, I feel it to be a great pleasure to thank you for your kindness and hospitality, and for the great honour you have done me in inviting me here to-night, and I am sure that all the other foreign guests will join me in my most cordial thanks to the Society for this honour.

It is, for me especially, a great pleasure to be present, as this Society represents the British chemical science which primarily gave the world the idea of the important problem of fixing the nitrogen of the air.

A hundred years ago Priestley and Cavendish discovered what Lord Rayleigh, Sir William Ramsay, and above all Sir William Crookes successfully developed.

In Professor Birkeland's and my work on the same problem, *these* names served as beacons in the atmosphere, and guided us on our way, so that we have *British* science to thank in many respects for our success in creating an industry upon the problem of the fixation of the nitrogen of the air.

Formerly your countrymen came over to Norway to view the scenery of our large waterfalls and mountains, but to-day we send these natural properties to this country, in the form of a fertiliser, to enrich your soils.

We have sent this product to almost all parts of the world, and it is particularly interesting to note that the results have proved better in the British Isles than anywhere else, and I can only regard the fact that the Norwegian air put into British soil gives such good results, as a sign of the strong feeling of sympathy which, I am proud to say, prevails between our countries.

I wish to conclude these words with the toast of the further prosperity of this famous and distinguished Society.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 17th, 1910.

Sir ARCHIBALD GEIKIE, K.C.B., President, followed by Mr. A. B. KEMPE, Vice-President, in the Chair.

PAPERS were read as follows:—

"*Effect of Gravity upon the Movements and Aggregation of* Euglena viridis, *Ehrb., and other Micro-organisms.*" By HAROLD WAGER, F.R.S.

Euglena viridis and some other micro-organisms, when placed in shallow vessels or narrow tubes in the dark, become aggregated into peculiar network-like patterns or more or less well-defined groups. In a narrow tube, placed horizontally in the dark, the aggregation takes the form of a series of groups which look like green bands crossing the tube from one side to the other. Each group shows a constant cyclic up and down movement, the denser central region moving downwards under the influence of gravity, and a lighter peripheral area consisting of organisms moving upwards, mainly by their own activity.

The aggregation depends upon the number of organisms present, their activity and the depth of the vessel in which they are contained, and may persist with its regular cyclic movements for several days.

The downward movement appears to be a purely mechanical one, dependent upon the specific gravity of the organism, and is not due to a stimulus which evokes a physiological response as in geotropism or geotaxis. The upward movement is, on the other hand, due partly to the activity of the organisms themselves, partly, no doubt, to the upward currents set up in the liquid by the friction of the downward moving stream. The upward movement of *Euglena* is more or less vertical, and appears to be controlled, so far as the orientation of its elongate body is concerned, by the action of gravity.

The aggregation resembles the cohesion figures produced when fine sediments are allowed, under certain conditions, to settle down slowly in a liquid, and are

probably brought about much in the same way. The movements of certain micro-organisms are apparently controlled, therefore, in a purely mechanical fashion by gravity, combined with cohesive forces, and this is of advantage to species which, like *Euglena*, are often found in large numbers in a confined space, in that it prevents their accumulation in such dense masses as would be likely to interfere with their assimilatory and respiratory functions.

"*Proteolytic Enzyme of Drosera.*" By Miss Jean White.

"*Influence of Bacterial Endotoxins on Phagocytosis (including a New Method for the Differentiation of Bacteria*"). Second Report. By Leonard S. Dudgeon, P. N. Panton, and H. A. F. Wilson.

We have failed to demonstrate in any of our experiments an action of the endotoxic substances on the leucocytes, and experiments leading to similar results were obtained by allowing bacteria to be exposed to the action of the specific endotoxic substances.

We confirm the results published in our first communication that the phagocytic result is dependent upon the interaction of endotoxin of serum. We have shown in the case of normal serum that the amount of phagocytosis permitted when bacteria and endotoxin interact is not related to the amount of hæmolytic complement present.

The action of endotoxin appears to be specific even with bacteria so closely related as the typhoid and paratyphoid family. These results strongly suggest that this method can be employed for the differentiation of bacteria. The amount of endotoxin has been shown to be strongly thermo-stable.

"*Investigations on the State of Aggregation of Matter.*" (Parts I.—III). By S. B. Schryver.

Part I. *The Action of Salts in Heterogeneous Systems and the Nature of the Globulins.*—When complex substances, such as those which form colloidal solutions, enter into chemical reaction, the ordinary laws of chemical mass action are not always obeyed, the deviations therefrom depending upon the medium in which the reaction takes place. These are due to the adsorption of molecules from the medium on the surface of the large molecules of the colloid, which sterically inhibit chemical reaction. These conclusions were deduced chiefly by the study of the action of formaldehyde on Witte's peptone, whereby a methyleneimino derivative is formed, which readily, either by polymerisation or condensation between two molecules, forms an insoluble complex. The formation of this complex is inhibited by the presence of salts, the inhibitory action of a series of which has been quantitatively measured. The degree of inhibition was found to depend, in the case of monobasic sodium salts, on the physical properties of their aqueous solutions. The lower the surface tension and the lower the viscosity of the solutions, the greater the inhibitory action. The effect of surface tension could be deduced from the general study of adsorption phenomena, whilst the effect of viscosity could be deduced by the extension of the generalisations of Whitney and Noyes, and of Nernst as to the reaction rates in heterogeneous systems.

The globulins, which are insoluble in water but soluble salt solutions, are assumed to be complexes formed by the action of a basic group in one molecule with an acid group in another, by means of which a salt is formed, which undergoes slight but definite hydrolytic dissociation in the presence of water. In the presence of most salts, owing to adsorption by the dissociated globulin molecules, hydrolysis proceeds further than in presence of water alone, with the consequence that more globulin is dissociated and "dissolved." The solvent action of the salts here again depends upon the surface tensions of the solutions.

Salts exert also a similar action in other heterogeneous systems in bringing about disaggregation, and the differences of solubility of various crystalline substances in salt solutions can be thereby explained.

The physical constants of the salt solutions employed, and the solubilities of edestin and serum globulin in these solutions, are given.

Part II.—*The Action of Formaldehyde on Witte's Peptone.*—The experimental details of this investigation are given. It is shown that the insoluble precipitate, formed by the interaction of the solutions, is derived chiefly from the more complex polypeptides.

Part III.—*The Solubility of Phenol and certain Crystalline Substances in Salt Solutions.*—The deductions as to the action of salts in heterogeneous systems are illustrated by the determination of the critical solution temperatures of phenol and salt solutions, which is a function chiefly of the surface tensions of the latter, and of the solubility of the following substances in salt solutions: *d. l.* leucine, *d. l.* phenylalanine, caffeine, benzamide, and *p.* toluidine. The solubilities are affected by both the surface tensions and viscosities of the solutions.

"*Method for Isolating and Growing the Lepra Bacillus of Man.*" By F. W. Twort.

Experiments were undertaken to obtain a method whereby the lepra bacillus of man and allied bacilli might be cultivated outside the body on artificial media.

The material tested was obtained from a typical leper. Cultivations were made on ordinary laboratory media and on media containing extracts from animal organs and tissues; these gave negative results.

In view of the close relationship between the tubercle bacillus and the lepra bacillus, it appeared highly probable that these two micro-organisms would require the same chemical substances for building up their protoplasm which could be elaborated from the ordinary media only by the tubercle bacillus. It was thought that if these substances could be supplied already formed to the lepra bacillus it might grow, and the easiest method of supplying these substances would be by adding to some good medium the ground up bodies of the tubercle bacilli containing them; accordingly a medium was made as follows:—

> Egg three parts, 0·8 per cent sodium chloride one part, ground tubercle bacilli 1 per cent and glycerin 5 per cent or less, mixed, placed in tubes sterilised and set in slopes.

Leprosy material was placed in 2 per cent ericolin to kill contaminating micro-organisms, and then inoculated on the tubercle medium. On this the lepra bacillus grew very slowly as a delicate colourless streak along the inoculated track, and showed the typical morphological and staining characters of the lepra bacillus; the bacillus could be sub-cultured only on the tubercle medium.

Experiments will be made to prepare a lepra vaccine and to grow the lepra bacillus of rat. In conjunction with Mr. Ingram I have also succeeded in growing the bacillus found in Jöhne's disease of cows. It grows on the same medium, much like lepra bacillus, but somewhat faster. We hope soon to prepare a diagnostic vaccine for Jöhne's disease.

"*Oxidation of Phenol by certain Bacteria in Pure Culture.*" By Gilbert J. Fowler, Edward Ardern, and William T. Lockett.

The investigation described in the paper arose out of a detailed examination of the effect of various antiseptic substances, including phenol, in bacterial sewage filters. It was found that the phenol apparently exerted a selective action on the bacteria present in the filter, only very few types appearing in the filtrate, more especially a liquefying organism (*B. liquefaciens fluorescens*) and a chromogenic organism.

Pure cultures of these organisms were made, the medium generally used being ordinary peptone broth. The general method of experiment was to bubble air, under sterile conditions, through an aqueous solution of phenol to which a few cc. of the culture were added. The strengths of phenol solution used varied from 8·4 to 16·5 parts phenol per 100,000 of water, and were determined by the oxygen absorbed from standard acid permanganate solution in three minutes.

It was found that *B. liquefaciens* had no action, or only a very slight one, on phenol, even after exposure of a month or more, while on introduction of the chromogenic organism, the phenol content diminished, slowly, at first, and then, in two or three days, completely disappeared.

In a final experiment, a solution was made use of, containing ten parts per 100,000 of phenol, together with the following ingredients: —

Ammonium sulphate	.. ..	0·1 grm. per litre.
Potassium phosphate	.. ..	0·1 ,,
Magnesium carbonate in suspension.	.. ..	½—1 ,,

After careful sterilisation, this was inoculated with the organism, and incubated. After nine days the phenol had practically disappeared. Plate cultures were also made at the expiration of this time, and showed no evidence of the presence of more than one species of organism.

The organism has been examined by Dr. Sidebotham, who concludes that it most nearly resembles *B. Helvolus* (Zimmermann).

CHEMICAL SOCIETY,

Ordinary Meeting, November 3rd, 1910.

Prof. Harold B. Dixon, M.A., Ph.D., F.R.S., President, in the Chair.

Messrs. Charles W. Meanwell and R. O'F. Oakley were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Bertram Haward Buttle, 63, Claremont Road, Forest Gate, E.; Frank Anthony Camp, care of Messrs. Parry and Co., Madras, India; David Chalmers Crawford, M.A., B.Sc., Elsenburg, Mulders, Vlei, Cape Colony; Arthur Dodd, Lyndhurst, Belvedere, Kent; Fred Holt, B.Sc., 28, Mere Street, Rochdale; Prince Mahmood Ali Khan, B.A., Zafermanzl, Rampur State, U.P. India; James Eckersley Myers, B.Sc,, Acresfield, Gatley, Cheshire; Sidney Herbert Newman, B.Sc., 181, Brooke Road, Upper Clapton, N.E.; Alfred Oswald Ransome, Beechwood, Greenock Road, Paisley; Rajendra Nath Sen, M.A., M.Sc., 41, Machuabazar Street, Calcutta; Arthur Bernard Williams, Coychurch Rectory, Bridgend, South Wales.

Of the following papers, those marked * were read :—

*276. "*Researches on Bleaching Powder.*" By Robert Llewellyn Taylor.

The author has investigated the action of carbon dioxide and on air on bleaching powder.

When carbon dioxide acts on bleaching powder, either solid or in solution, nothing but chlorine is evolved. The conclusion is drawn that the action of carbonic acid is exactly like the action of any other acid, hydrochloric and hypochlorous acids being produced and decomposing each other with the liberation of chlorine. Hence the action of hydrochloric acid on carbonates is a reversible one.

Air free from carbon dioxide sweeps out very slowly a little hypochlorous acid from a solution of bleaching powder. This is due to the hydrolysis of the hypochlorite in the solution. Ordinary moist air liberates from solid bleaching powder at first a mixture of hypochlorous acid and chlorine, and finally nothing but chlorine. In aqueous solution the action is almost the same.

It was shown that the action of bromine on alkalis is a reversible one, and the conclusion is drawn that the action of chlorine is the same. The carbon dioxide in air unites with the free lime, and then the calcium chloride present reverses the action, liberating chlorine.

Air free from carbon dioxide expels a considerable amount of chlorine from a solution of bleaching powder, from which some of the free lime has been removed. Such a solution bleaches more rapidly than an ordinary solution, and calcium chloride or salt added to it helps to reverse the action, liberating more chloride, and further stimulating the bleaching action. In the ordinary bleaching process, chlorine is probably the active bleaching agent, hypochlorous acid only playing a minor part.

Discussion.

The President asked whether the author thought it necessary to assume that carbonic acid had the power of decomposing sodium or calcium chloride, when he had shown that carbonic acid liberated chlorine from a solution of bleaching powder by combining with the free hydrate, and so reversing the action of chlorine on calcium hydrate : $2Ca(OH)_2 + 2Cl_2 \rightleftharpoons CaCl_2 + Ca(OCl)_2 + 2H_2O$.

Dr. Senter, referring to the author's view that carbon dioxide liberates both hydrochloric and hypochlorous acids from bleaching powder, said that it did not seem justifiable to adduce as evidence in favour of this suggestion the fact that carbon dioxide turns methyl-orange red in presence of sodium chloride. It could be shown (compare Bohdan von Szyszkowski, *Zeit. Phys. Chem.*, 1910, lxxiii., 273) that, so far as purely chemical interchange between the components is concerned, the hydrogen-ion concentration in a solution containing carbon dioxide and sodium chloride is less than for the carbon dioxide alone in water. The observed effect on methyl-orange must therefore be ascribed to some other factor, doubtless to the so-called "neutral salt action" illustrated, for example, by the observation of Arrhenius that the catalytic action of acetic acid is increased by the addition of salts, such as sodium chloride. In the present case the neutral salt probably acts by increasing the dissociating power of the medium. The effect on methyl-orange is therefore to be ascribed to increased ionisation of the carbonic acid in the salt solution, and not to the liberation of hydrochloric acid from the sodium chloride.

Prof. Green could confirm Mr. Taylor's view of the reversibility of the reaction between halogens and alkalis, at least in the case of bromine and iodine. Thus an alkaline solution of iodine gave the starch reaction even in presence of a considerable excess of alkali hydroxide.

Mr. Taylor, in reply, stated that whilst he had shown that the carbon dioxide in the air caused the liberation of chlorine in the way described, yet the action of pure carbonic acid on bleaching powder was so very much more rapid than that of air that it suggested a complete decomposition (such as is produced by other acids) rather than the reversed action which was induced by the removal of the free lime. The equation quoted by the President did not necessarily represent what took place when bleaching powder was made, but simply the condition of equilibrium in which it existed in solution.

*277. "*Azomethineazo-dyes.*" By Arthur George Green and Rajendra Nath Sen.

In order to investigate the effect on the colour and dyeing properties brought about by the simultaneous presence in a compound of the azomethine and azo-groups, the authors have prepared and examined a number of dyes obtained by condensing phenetoleazobenzaldehydesulphonic acid, $OEt{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(SO_3H){\cdot}CHO$, with various amines and diamines. These compounds, of various complexity, are all yellow crystalline products, which dye wool readily in fast shades. Affinity for cotton is only manifested when the compound is derived from a para-diamine. The introduction of an auxochromic group (OH or NMe_2) has practically no effect on the dyeing properties, and does not increase the tinctorial power, augment the affinity, or change the shade. Moreover, the colour is almost independent of the number of azomethine groups in the molecule. The members of the series which do not contain an auxochromic group possess, like the azo-dyes of the stilbene class, to which they have some structural analogy, a considerable degree of fastness to to alkalis, light, and chlorine.

Discussion.

Prof. Green said, in reply to Dr. Cain, that the colour of the azomethineazo-dyes was uninfluenced by the intro-

duction of naphthalene nuclei in the molecule. The ethoxy-group did not act as an auxochrome in these compounds. Ethoxy-groups apparently only exhibited auxochromic action when they could act as salt-forming groups by combination with acids.

*278. "*Syntheses in the Epinephrine Series.* Part II. *The Formation and Properties of some* 2 : 5- *and* 2 : 6-*Substituted Pyrazines and their Conversion into Amino-ketones and Imino-diketones.*" By Frank Tutin.

ω - Chloroacetophenone, ω - chloro - *p* - methoxyacetophenone, and *ω-chloro*-mp-*dimethoxyacetophenone*, when heated with ammonia, yield mixtures of 2 : 5 and 2 : 6-substituted pyrazines. The two series of reactions involved proceed as follows, after replacement of the halogen : —

$$2R\cdot CO\cdot CH_2\cdot NH_2 \rightarrow N\leqq \begin{matrix} CR\cdot CH_2 \\ CH_2\cdot CR \end{matrix} \geqq N \rightarrow$$

$$\rightarrow N\leqq \begin{matrix} \cdot CR{:}CH \\ \cdot CH{:}CR \end{matrix} \geqq N$$

$$(R\cdot CO\cdot CH_2)_2NH + NH_3 \rightarrow NH\leqq \begin{matrix} CR{:}CH \\ CR{:}CH \end{matrix} \geqq NH \rightarrow$$

$$\rightarrow N\leqq \begin{matrix} CR{:}CH \\ CR{:}CH \end{matrix} \geqq N$$

2 : 5 - Diphenylpyrazine, 2 : 6 - diphenylpyrazine, pp'-*dimethoxy* - 2 : 5 - *diphenylpyrazine*, pp' - *dimethoxy* - 2 : 6 - *diphenylpyrazine*, mm'pp' - *tetramethoxy* 2 : 5 - *diphenyl pyrazine*, and mm'pp'-*tetramethoxy*-2 : 6-*diphenylpyrazine* have thus been prepared.

The reactions represented above can be reversed : by treatment with hydriodic acid the pyrazine derivatives mentioned yield respectively the *hydriodides* of the following bases : —*ω*-Aminoacetophenone, diphenacylamine, *ω*-amino-*p*-hydroxyacetophenone, pp'-*dihydroxydiphenacylamine*, *ω*-amino-*mp*-dihydroxyacetophenone, and mm'pp'-*tetrahydroxydiphenacylamine*.

Diphenacylamine and its derivatives, when heated with ammonia, yield 2 : 6-substituted pyrazines.

ω - Chloro-o-methoxyacetophenone and *ω - chloro*-op-*dimethoxyacetophenone* yield only resinous products when heated with ammonia, but through the agency of potassium phthalimide, salts and derivatives of *ω-amino-o-hydroxyacetophenone* and *ω-amino*-op-*dihydroxyacetophenone* have been prepared from these chloro-ketones.

The last-mentioned two bases. when dissolved, pass spontaneously into oo'-*dihydroxy*-2 : 5-*diphenylpyrazine* and oo'pp'-*tetrahydroxy*-2 : 5-*diphenylpyrazine* respectively.

All the hydroxy-ketonic bases mentioned, with the exception of *ω*-amino-*o*-hydroxyacetophenone, are physiologically active.

pp'-Dihydroxy-2 : 5-diphenylpyrazine, on fusion, passes into a "liquid-crystalline" state, which persists over a range of 41·4°.

Numerous salts and derivatives of the compounds mentioned above were described.

*279. "*The Absorption Spectra of some Substituted Pyrazines and their Salts.*" By Frank Tutin and Frederic William Caton.

The authors have examined the absorption spectra of 2 : 6 - diphenylpyrazine, *pp'* - dimethoxy - 2 : 6 - diphenylpyrazine, and *mm'pp'*-tetramethoxy-2 : 6-diphenylpyrazine, and of the monohydrochlorides and monohydrobromides of these bases. 2 : 5-Diphenylpyrazine and its monohydrochloride, and *pp'*-dimethoxy-2 : 5-diphenylpyrazine and the corresponding salts of this base have also been examined spectroscopically.

A number of mono- and di-acid salts of the above-mentioned bases, and of *mm'pp'*-tetramethoxy-2 : 5-diphenylpyrazine were described.

*280. "*Studies in the Camphane Series.* Part XXVIII. *Stereoisomeric Hydrazones and Semicarbazones of Camphorquinone.*" By Martin Onslow Forster and Adolf Zimmerli.

The *α*- and *β-camphorquinonehydrazines*,—

$$C_8H_{14}\begin{matrix} C{:}N\cdot NH_2 \\ | \\ CO \end{matrix},$$

produced simultaneously by the action of hydrazine hydrate on the diketone, and melting at 206° and 102° respectively, are interconvertible by heat. Phenylcarbimide transforms them into the *α*- and *β-camphorquinone-phenylcarbamylhydrazones*,—

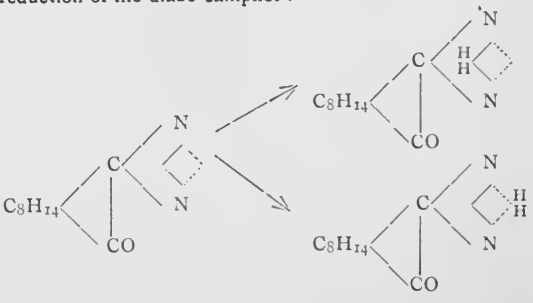
$$C_8H_{14}\begin{matrix} C{:}N\cdot NH\cdot CO\cdot NH\cdot C_6H_5 \\ | \\ CO \end{matrix},$$

melting at 211° and 161° respectively, a mixture of which is produced by the condensation of camphorquinone with phenylcarbamylhydrazide, and also by the action of hot aniline on the camphorquinonesemicarbazones. One of the last-named substances, the *α*-compound, has been already described by Lapworth and Chapman (*Trans.*, 1901, lxxix., 381), and melts at 236°, whilst the *β-camphorquinonesemicarbazone*, $C_8H_{14}\begin{matrix} C{:}N\cdot NH\cdot CO\cdot NH_2 \\ | \\ CO \end{matrix}$, melts at 147°, and is converted into the *α*-modification at temperatures between these melting.points. Each semicarbazone is transformed into the acetyl derivative of the corresponding hydrazone by hot acetic anhydride, and of these the *α-acetylhydrazone* (m. p. 239°) is changed into the *β-acetylhydrazone* (m. p. 150°) by acetic anhydride, the converse transformation being effected by heat.

Both hydrazones are oxidised immediately to diazocamphor by cold aqueous mercury acetamide, and they are both regenerated from the diazo-compound by reduction with alcoholic ammonium sulphide. In view of these relationships, and since the members of each pair of hydrazones, semicarbazones, and phenylcarbamylhydrazones differ but little from one another in optical activity, whilst the only chemical distinction hitherto brought to light is the transformation of the *β*-semicarbazone into camphane-oxytriazine by alkalis, which leave the *α*-semicarbazone unaltered, the authors believe that stereoisomerism prevails in this group, and that their experiments give support to the Hantzsch-Werner hypothesis.

Discussion.

Mr. W. Robertson submitted that the authors had not proved their case. In the first instance, the conclusion drawn that the *α*- and *β*-compounds were not polymerides had yet to be definitely established; the wide differences in solubility and in melting-point were at variance with this conclusion. Exception was also taken to the dismissal of the "phane" formula for the hydrazone on the evidence available. Moreover, if the Hantzsch-Werner tetrahedral configuration of the nitrogen atom, postulated by the authors, were examined, there were two "phane" hydrazones possible according to the linking broken on the reduction of the diazo-camphor :—



Thus there should be four, not two, isomeric hydrazones of camphorquinone capable of existence on this hypothesis. Another constitution for a hydrazone was suggested as

worthy of consideration, namely, $\begin{matrix}\cdot C \text{——} \cdot N \\ | \quad\quad | \\ \cdot C(OH) \cdot NH\end{matrix}$, as this "carbonyl-ammonia" derivative might be expected to react like a hydrazone of the constitution $\begin{matrix}\cdot C{:}N \cdot NH_2 \\ | \\ \cdot CO\end{matrix}$.

Dr. Forster did not agree that two "phane" hydrazones are possible, being under the impression that according to Hantzsch and Werner the tetrahedral configuration of the nitrogen atom is supposed to apply only to those cases in which that element is multiple-linked with another atom, so that on adding hydrogen to diazocamphor the nitrogen valency-directions would distribute themselves in one plane.

(To be continued).

NOTICES OF BOOKS.

Principles of Chemical Geology. By James Vincent Elsden, D.Sc. (Lond.), F.G.S. London and New York: Whittaker and Co. 1910.

In this book the results obtained by the application of the principle of equilibrium to some important geological problems are described in detail, and such debated questions in geology as appear likely to be solved by the methods of physical chemistry are briefly discussed. The author believes that the determination of the equilibrium conditions will give the clue to the complete elucidation of many problems in geology. He therefore considers viscosity, diffusion, surface tension, vapour pressure, in succession as factors of equilibrium, and in addition gives a summary of the eutectic theory and the theory of solid solutions as far as they are of importance in geology. He shows excellent judgment and moderation in stating the views of other workers whose researches he has evidently carefully studied, and his expositions are clear and detailed. It seems not improbable that it would require a greater knowledge of chemistry than the average specialist in geology might be expected to possess, in order to study the book with the utmost profit, but, on the other hand, it is difficult to see how such an intricate subject could have been treated more simply and from a more elementary point of view.

Dangerous Goods. By Dr. Julius Aeby. Published by the Author: Antwerp. 1910.

The author of this volume, who for many years has acted as expert adviser to shipping and railway companies on questions relating to the transport of dangerous goods, has had unique opportunities of acquiring experience about the precautions to be observed and the dangers to be feared in such transport, and has endeavoured in this book to make his special knowledge more accessible to those interested in the subject. The book gives the French, English, and German names of all commercial products which may be regarded as dangerous to handle in bulk, either because they are poisonous, inflammable, corrosive, explosive, or evil-smelling. The physical properties of each substance are enumerated in all three languages, and the exact conditions in which each is dangerous are described.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th instant, Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Prof. Emanuele Paterno di Sessa (Rome), Prof. Dr. Emil Gabriel Warburg (Charlottenburg), Prof. Jules Henri Poincaré (Paris), Prof. Alexander Graham Bell (Washington), and Prof. Pëtr Nikolájewitsch Lebedew (Moscow), were elected Honorary Members of the Institution. Mr. H. Rudston Read and Mr. W. A. Tanner were elected Members.

CORRESPONDENCE.

ACADEMIC STATUS OF THE F.I.C.

To the Editor of the Chemical News.

Sir,—The qualifications of the Institute of Chemistry enjoy full recognition of their merits in certain scientific and industrial circles, and by certain authorities, such as the Government, but we are convinced that the value of the qualifications is not appreciated by local educational authorities, nor, indeed, by the public at large. Too frequently is the F.I.C. mistaken for the membership of some society carrying with it no professional status and gained merely by election and the payment of a fee. Having regard to the strict regulations as to training and to the very severe examinations—more difficult than University honours—imposed upon candidates for the Institute, we feel that an effort should be made to secure for members of the Institute in general, and those engaged in academic work in particular, a fuller recognition of their qualifications.

We are of opinion that if the privilege of wearing academic dress were conferred upon members of the Institute it would do *something* towards distinguishing the F.I.C. as a qualification of academic standing. We have been in communication with the Council of the Institute, and we have been informed that if there is any considerable support to the proposal they will give the matter consideration. We should be glad, therefore, if all Fellows and Associates, whether the privilege would be of any direct benefit to them or not, who think that a regulation by the Council upon this question might help to raise the F.I.C. in the estimation of the public, and are therefore in favour of the proposal, would send their names to Mr. V. H. Kirkham, Galleywood, Chelmsford.

We should be much obliged to you, Sir, if you would give this matter notice in your paper.—We are, &c.,

Vincent H. Kirkham, B.Sc.(Lond.), F.I.C.
J. Hembrough, A.R.C.Sc., A.I.C.
James Hart-Smith, A R.C.Sc., F.I.C.

Galleywood, Chelmsford,
November 22, 1910.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cli., No. 15, October 10, 1910.

Reduction of Iron Oxide by Solid Carbon.—G. Charpy and S. Bonnerot.—Graphite and iron sesquioxide were purified, ground together in a mortar, and agglomerated by a pressure of several thousands of atmospheres. The mixture was then heated at varying pressures, and the volume of gas generated in a given time was measured. It was found that at 950° the velocity of the reaction rapidly diminishes with the pressure, and practically vanishes when the pressure is of the order of 1/1000 mm. of mercury. Thus solid carbon does not reduce iron oxide, at any rate until a temperature of 950° is reached.

Presence of Small Quantities of Carbon Monoxide in the Air of Coal-mines.—P. Mahler and J. Denet.—Determinations of the carbon monoxide in the air of coal-mines, using iodic anhydride, showed the presence of an average of 0·002 per 100 volumes. The highest amount found was 0·004. The maximum occurred with a minimum of fire-damp, and the minimum with a maximum of fire-damp.

No. 16, October 17, 1910.

Relative Durations of Spectral Rays emitted by Magnesium Vapour in the Electric Spark.—G. A, Hemsalech.—By determining the duration of the rays of magnesium vapour for two different values of the capacity, it was found that the rays of the nebulous series are more affected by variations of the capacity than those of the triplets. Most impurities show durations which are abnormal when referred to their intensities, and this renders the identification of impurities very easy.

Influence of Chemical Affinity in some so-called Adsorption Phenomena.—Léo Vignon.—Experiments with silica, alumina, oxide of zinc, &c., and various dissolved colouring matters (picric acid, fuchsine S) show that insoluble solids do or do not fix dissolved colouring matters according to the chemical functions present. Thus chemical affinity is the force which determines the fixation by certain surfaces of substances which are actually dissolved in fluids (liquids or gases), and the so-called adsorption phenomena may be divided into two distinct classes—substances in false solution or suspension are fixed by special attraction, and those which are really dissolved are fixed by chemical affinity.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xliii., No. 14, 1910.

Stereochemistry of Pentavalent Nitrogen. — M. Scholtz.—It has already been observed that two stereoisomers are obtained when an asymmetric pentavalent nitrogen atom is formed by the union of a halogen alkyl with an optically active tertiary base. From theoretical reasons it is to be expected that two inactive compounds would result if an inactive base with an asymmetric carbon atom were made to unite with an inactive halogen alkyl, if the nitrogen atom were thus made asymmetric. This was confirmed by the isolation of two quaternary ammonium iodides from inactive N-ethylmethyl-phenylpiperidine and allyl iodide. *o*-Xylylene bromide gives with methyl phenyl piperidene two isomeric compounds in which the nitrogen atom belongs to two ring systems, and both the carbon atoms of the piperidine ring next to the nitrogen are asymmetric.

Detection of Small Amounts of Cyanogen.—Georg Lockemann.—The substance is mixed with dilute sulphuric acid and heated. The tube in which it is heated is closed by a piece of filter-paper which has been soaked in caustic potash or soda. The HCN evolved if CN is present is absorbed by the caustic potash, and if ferrous sulphate solution is added after a short time the greenish precipitate of ferrous hydroxide becomes brown owing to the formation of ferric hydroxide. On the addition of hydrochloric acid and water-vapour the characteristic Berlin blue appears. Cyanogen can also be detected by the rhodan-test. The filter-paper in this case is treated with ammonium sulphide. The paper is exposed to the fumes from the solution to be tested, and is then acidified with hydrochloric acid. The appearance of a red coloration on the addition of ferric chloride solution shows the presence of cyanogen.

Acetato-pyridine Iron Base and a very Basic Ferric Acetate containing Pyridine.—R. Weinland and E. Gussmann.—When pyridine acts on the acetate of the hexacetato-triferric base an acetato-ferric base containing pyridine is obtained. From this base salts containing two atoms of iron and two molecules of pyridine can be isolated. When pyridine acts on the aqueous solution of the monacetate of the triferric base at certain definite concentrations a very basic crystalline ferric acetate containing pyridine is obtained. Its formula is: $Fe_2O(OH)(CH_3COO)_3.C_5H_5N$.

Nitrous Oxide.—A. Stavenhagen and E. Schuchard.—Strongly heated sulphur burns in a current of nitrous oxide, giving nitrosulphonic acid anhydride and nitrogen: $2S + 9N_2O = O{<}\begin{matrix}SO_2.NO_2\\SO_2.NO_2\end{matrix} + 8N_2$. When a little water is added nitrogen trioxide is obtained: $N_2S_2O_9 + 2H_2O = 2H_2SO_4 + N_2O_3$, while with more water the following reaction occurs: — $3N_2S_2O_9 + 7H_2O = 6H_2SO_4 + 2HNO_3 + 4NO$. In presence of water nitrosyl sulphuric acid is formed: $2S + H_2O + 9N_2O = 2SO_2{<}\begin{matrix}OH\\NO_2\end{matrix} + 8N_2$. In the vessel after the experiment the following products were detected: —Sulphuric acid, sulphurous acid, nitric acid, and nitrous acid. Thus the conversion of nitrous oxide into higher oxides of nitrogen can be effected without the application of electrical energy.

Preparation of Aromatic Alcohols and their Acetates.—A. Wohl and E. Berthold.—Already noticed.

New Compounds of Tetravalent Cerium.—G. A. Barbieri and J. Calzolari.—Cerous salts can be oxidised to ceric salts by means of nitric acid only if (i.) the cerous salt is soluble in nitric acid. (ii.) The acid of the cerous salt is not volatile and does not react with nitric acid. (iii.) The ceric salt is insoluble or only slightly soluble in nitric acid. By this method of oxidation the authors have prepared ceric selenite, $Ce(SeO_3)_2$, and the acid ceric arsenates $Ce(H_2AsO_4)_4$ and $Ce(HAsO_4)_2$. The selenite, like all ordinary ceric salts, is orange-yellow, the compound $Ce(HAsO_4)_2$ is white with a tinge of yellow, and $Ce(H_2AsO_4)_4$ is snow-white.

Double Rhodanides of Divalent Copper and Cobalt with Organic Bases. – J. Calzolari.—Already noticed.

Triazol and Tetrazol from Hydrazoic Acid.—Otto Dimroth and Gustav Fester.—With acetylene triazoic acid gives 1.2.3-triazol, and with hydrocyanic acid tetrazol. Diazo-methane and diazo-acetic ester give with acetylene and acetylene derivatives pyrazol and its derivatives, the reactions occurring very easily. Hydrazoic acid is less active, and must be heated in a closed tube with acetylene in acetone solution for about seventy hours to 100° in order that the condensation may be effected. In these circumstances phenylazide gives with acetylene 1-phenyl-2:3-triazol. Diazomethane reacts easily with hydrocyanic acid, yielding not triazol but carbylamine and acetonitrile. In alcohol solution with anhydrous hydrocyanic acid hydrazoic acid gives tetrazol, while phenylazide does not unite with hydrocyanic acid.

MISCELLANEOUS.

Physical Society.—The Sixth Annual Exhibition of Electrical, Optical, and other Physical Apparatus will be held at the Imperial College of Science, Imperial Institute Road, South Kensington, on Tuesday, December 20th, 1910, from 3 to 6 p.m., and from 7 to 10 p.m. Dr. J. A. Fleming, F.R.S., will give a short experimental discourse on "Detectors" in the afternoon and also at the Evening Session. Admission will be by ticket only. A ticket and programme will be sent to every Fellow in due course. Further tickets can be obtained from Mr. W. R. Cooper, 113, Tulse Hill, S.W.

Royal Society.—At the Annual Meeting on November 30th, 1910, the following were elected Members of the Council of the Royal Society for the ensuing year:—President—Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., LL.D. Treasurer—Alfred Bray Kempe, M.A., D.C.L. Secretaries—Sir Joseph Larmor, D.Sc., D.C.L., LL.D.; John Rose Bradford, M.D., D.Sc. Foreign Secretary—Sir William Crookes, O.M., D.Sc. Other Members of the Council—Lazarus Fletcher, M.A.; Walter Holbrook Gaskell, M.D.; Sir David Gill, K.C.B.; Prof. Ernest Howard Griffiths, Sc.D.; Prof. William Mitchinson Hicks, D.Sc.; Prof. F. Stanley Kipping, D.Sc.; Major Percy Alexander MacMahon, Sc.D.; Henry Reginald Arnulph Mallock; Charles James Martin, M.D.; The Duke of Northumberland, K.G.; Prof. William Jackson Pope, F.C.S.; Prof. John Henry Poynting, D.Sc.; Prof. Ernest Rutherford, D.Sc.; Arthur Everett Shipley, M.A.; M. R. Oldfield Thomas, F.Z.S.; Harold W. T. Wager. F.L.S.

Royal Society of Arts Albert Medal.—At the request of the Council of the Royal Society of Arts, Sir Edward Grey, Secretary of State for Foreign Affairs, authorised the transmission of the Society's Albert Medal to His Majesty's Ambassador at Paris for its presentation to Mdme. Curie. Sir Francis Bertie received Mdme. Curie at the British Embassy on November 25th, and handed to her the Albert Medal, telling her that he had been instructed by the Secretary of State to present it to her on the part of the Royal Society of Arts in recognition of the services rendered to the world by her discovery of radium, and adding that it gave him great pleasure to be the medium of carrying out the wishes of the Society.

Royal Institution.—The following are the lecture arrangements of the Royal Institution before Easter:—Prof. Silvanus P. Thompson, a Christmas Course of six illustrated lectures on "Sound, Musical and Non-musical," a course of experimental acoustics, adapted to a juvenile auditory—(1) Production of Sound, (2) Transmission of Sound, (3) Reception of Sound, (4) Combination of Sounds, (5) Registration of Sounds, (6) Reproduction of Sound; Prof. F. W. Mott, Fullerian Professor of Physiology, R.I., six lectures on "Heredity"; Dr. A. E. H. Tutton, three lectures on "Crystalline Structure—Mineral, Chemical, and Liquid"; Dr. M. Aurel Stein, three lectures on "Explorations of Desert Sites in Central Asia"; The Astronomer Royal, Mr. F. W. Dyson, three lectures on "Recent Progress in Astronomy"; Dr. P. Chalmers Mitchell, three lectures on "Problems of Animals in Captivity"; Mr. A. C. Benson, two lectures on "Ruskin"; Prof. Arthur Keith, two lectures on "Giants and Pygmies"; Prof. W. A. Bone, two lectures on "Surface Combustion and its Industrial Applications"; Mr. Arthur Hassall, three lectures on "Problems in the Career of the Great Napoleon"; Mr. T. G. Jackson, R.A., three lectures on "Architecture—the Byzantine and Romanesque Period"; Prof. Sir J. J. Thomson, Professor of Natural Philosophy, R.I., six lectures on "Radiant Energy and Matter." The Friday Evening Meetings will commence on January 20, when Prof. Sir James Dewar will deliver a Discourse on "Chemical Change at Low Temperatures." Succeeding Discourses will probably be given by Prof. W. H. Bragg, Mr. A. E. Shipley, Prof. H. E. Armstrong, Prof. Jean Perrin, Prof. Karl Pearson, Mr. J. H. Balfour-Browne, Sir David Gill, Prof. H. S. Hele-Shaw, Prof. Sir J. J. Thomson, and other gentlemen.

MEETINGS FOR THE WEEK.

MONDAY, 12th.—Royal Society of Arts, 8. (Cantor Lecture). "Industrial Pyrometry," by C. R. Darling.

TUESDAY 13th.—Faraday Society, 8. "Separation of Oxygen by Cold," by J. Swinburne. "New Apparatus for the Rapid Electro-analytical Determination of Metals," by H. J. S. Sand and W. M. Smalley. Exhibition of some New Pyrometers and Resistance Thermometers, and some Low- and High-reading Ampère-meters, &c., by R. W. Paul.

WEDNESDAY, 14th.—Royal Society of Arts, 8. "New View of Roman London," by R. A. Smith, B.A.

THURSDAY, 15th.—Royal Society of Arts, 4.30. "The Taj Mahal and its Relation to Indian Architecture," by R. F. Chisholm, F.R.I.B.A.

—— Chemical, 8.30. "Studies on Enzyme Action—Part XV., Comparative Influence of Monohydric C_nH_{2n+1} Alcohols and other Non-electrolytes on Enzymic Activity." by H. E. and E. F. Armstrong; Part XVI., "The Enzymes of Emulsin II., Prunase"; Part XVII., "The Enzymes of Emulsin III., Probable Seat of Origin of Amygdalin"; Part XVIII., "Enzymes of the Emulsin Type II., Distribution of β-Glucases in Plants," by H. E. and E. F. Armstrong and E. Horton; Part XIX., "Enzymes of the Emulsin Type III, Linase," by H. E. Armstrong and J. V. Eyre. "Interaction of Alloxan and Glycine," by W. H. Hurtley and W. O. Wooton. "Traube's Molecular Volume Method applied to Binary Mixtures of Organic Substances," by W. R. G. Atkins. "Investigations on the Dependence of Rotatory Power on Chemical Constitution—Part I., Rotations of the Simplest Secondary Alcohols of the Fatty Series," by R. H. Pickard and J. Kenyon. "Oxycodeine, a New Alkaloid from Opium," by J. J. Dobbie and A. Lauder.

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THE CHEMICAL NEWS

Vol. CII., No. 2664.

THE ATOMIC WEIGHT OF TANTALUM.*

By CLARENCE W. BALKE.

Introduction.

Of the previous determinations of the atomic weight of this element, those by Berzelius (*Pogg. Ann.*, 1825. iv., 14). Rose (*Pogg. Ann.*, 1856, xcix., 80), Hermann (*Journ. Prakt. Chem.*, 1857, lxx., 193), and Blomstrand (*Acta Univ. Lund*, 1864) need not be considered, as their material was too impure to give results of value. The determinations of Marignac, which appeared in 1866 (*Arch. Sci. Phys. Nat.*, 1866, [2], xxvi., 89 ; also *Journ. Prakt. Chem.*, xcix., 23), were far more satisfactory. He analysed potassium fluotantalate, K_2TaF_7, and the corresponding ammonium salt, $(NH_4)_2TaF_7$. In the case of the potassium salt he obtained the following percentages:—Ta_2O_5, 56·50, 56·75, 56·55, 56·56 ; K_2SO_4, 44·37, 44·35, 44·22, 44·24.

The ammonium salt gave the following percentages of tantalum oxide :—63·08, 63·24, 63·27, 63·42. These numbers were corrected for a small amount of potassium sulphate which was present in the oxide, due to the fact that he was unable to prepare the ammonium fluotantalate free from traces of the potassium salt.

If in the calculations the atomic weights of the elements involved are taken as given in the 1910 International Table the following values for the atomic weight of tantalum are obtained :—

From the ratio	$K_2TaF_7 : Ta_2O_5$	182·4 to 184 6
„ „	$K_2TaF_7 : K_2SO_4$	181·6 to 182·9
„ „	$K_2SO_4 : Ta_2O_5$	181·9 to 183·0
„ „	$(NH_4)_2TaF_7 : Ta_2O_5$ ..	180·5 to 183·8

It will be observed that there is a variation of several whole units between the individual determinations, yet for about forty years the accepted value of this constant was based on these results.

In 1906 Hinrichsen and Sahlborn published a series of determinations in which metallic tantalum was burned to the oxide (*Ber.*, 1906, xxxix., 2600). The method has great simplicity, but it appears very doubtful to the writer if this metal can be prepared sufficiently pure for the purposes of atomic weight work. Their results are given below.

Here again there is a variation of over one unit between the individual determinations. Clarke, after reviewing these various determinations of the value of this constant, remarks that its uncertainty probably amounts to as much as a unit ("A Re-calculation of the Atomic Weights," Smithsonian Miscellaneous Collections, 1910, liv., No. 3).

Wt. of Ta.	Wt. of Ta_2O_5.	Per cent O.	At. wt. Ta.
0·37200	0·45437	22·12	180·65
0·41278	0·50364	22·01	181·77
0·33558	0·40975	22·10	180·98
0·35883	0·43807	22·08	181·14
0·47554	0·58087	22·15	180·59
		Mean	181·03

While carrying out an investigation on columbium (Balke and Smith, *Journ. Am. Chem. Soc.*, 1908, xxx., 1637) it was found possible to make a satisfactory determination of the atomic weight of that element through the conversion of its pentachloride into the corresponding oxide. Consequently the writer decided to carry out a similar investigation with tantalum chloride, and, in general, the methods used were very similar to those employed in the former work.

* Presented at the San Francisco meeting of the American Chemical Society. From the *Journal of the American Chemical Society*, xxxii., No. 10.

Preparation of Materials.

In the preparation of all materials used during the investigation great care was exercised in the cleaning of all containing vessels, and especial care was taken to exclude dust. Whenever possible the apparatus used was made continuous by fusing the various parts together, and this was always the case where chlorine was being used. In the case of chemicals not especially purified, those of the highest purity obtainable were employed.

Chlorine.—The chlorine used, including that used in the preparation of the sulphur monochloride, was made by allowing hydrochloric acid to drip upon potassium permanagate contained in a large flask. The acid used was prepared by distilling the constant boiling mixture from large Jena retorts. During the first part of the distillation small quantities of potassium permanganate were added from time to time, and the first portions of the distillate were rejected. The chlorine was passed through a wash bottle containing water, two containing sulphuric acid, and finally through a tower 1 metre long containing glass pearls, and so arranged that the latter could be moistened from time to time with concentrated sulphuric acid.

Sulphur Monochloride.—This compound was prepared by passing a stream of chlorine over molten sulphur which had been crystallised previously from carbon disulphide. The apparatus was so constructed that the liquid could be re-distilled from the receiver without transferring the material. The first portions of the distillate were rejected, and the final product was collected directly in sealing flasks through which a stream of dry filtered air had been allowed to flow.

Nitric Acid.—The nitric acid used in the determinations was distilled twice from a platinum retort, the middle third of the distillate being retained in each case. The acid was preserved in quartz flasks.

Water.—The water used, including that employed in the final re-crystallisations of the potassium fluotantalate, was prepared by re-distilling the ordinary distilled water of the laboratory, after the addition of alkaline permanganate, from a still ordinarily used in the preparation of conductivity water.

Tantalum Chloride.—This compound was prepared by the ignition of tantalum oxide in a current of chlorine, and the vapours of sulphur monochloride. The oxides used for preparations I. and II. was prepared from some of the potassium fluotantalate which had been obtained by Hall and Smith from the columbite of South Dakota (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1369), and which was very kindly furnished me by Prof. Edgar F. Smith. (The author wishes to take this opportunity to express his appreciation for this and many other kindnesses shown him by Prof. Smith). This salt was re-crystallised four times from water containing appreciable amounts of re-distilled hydrofluoric acid, and only the first crops of crystals were used in the next crystallisation. These operations were carried out in platinum and hard rubber dishes, and hard rubber funnels were used in the filtration of the solutions. The final crop of crystals was heated in platinum dishes with concentrated sulphuric acid, which had been distilled from platinum, until most of the acid had been expelled. The residue was washed by decantation with large amounts of pure water. After this washing was complete, the mass was strongly ignited in platinum or quartz crucibles. Tantalum oxide prepared in this way has been shown to be pure (Balke, *Journ. Am. Chem. Soc.*, xxvii., 1140).

The oxide used for the third preparation of the chloride was obtained from the columbite of South Dakota as follows :—The finely ground mineral was fused with potassium hydroxide in large iron crucibles ; the mass was dissolved in water, and the solution, after filtration, was treated with sulphuric acid, which precipitated the metallic acids. These were washed with water by decantation, and then dissolved in an excess of hydrofluoric acid. The addition of potassium hydroxide to this solution gave a precipitate of potassium fluotantalate. (My thanks are due to one of my students, Mr. Lloyd Almy, who carried out

this preliminary work). The final purifications were carried out as previously outlined.

The apparatus used for the preparation of the chloride is shown in Fig. 1. The tantalum oxide (50—100 grms.) was introduced into the hard Jena glass tube H, the ends of which were connected with the bulbs E and I by means of carefully ground joints which were lubricated with a trace of graphite. These joints were wrapped with several thicknesses of asbestos paper, and the bulb of a thermometer was inserted in the latter at G, and the temperature regulated so as to prevent a deposition of the chloride at this point. A stream of chlorine was passed through the apparatus by means of the tube B for three to four hours, the entire apparatus being heated with a free flame in order to remove any traces of moisture which might be present. At this time the tube H containing the oxide was heated to a low red heat for the same purpose. Sulphur monochloride was then run into the bulb E through C, and heated to boiling. The oxide was slowly converted directly into the chloride, which together with the excess of sulphur monochloride collected in bulb I. When all of the oxide had been converted into chloride, leaving practically no residue in the tube H, the sulphur monochloride was driven on through the entire apparatus, and collected in O. The tantalum chloride was then distilled over into the bulb J, and the apparatus sealed off at L. The two-way stopcock

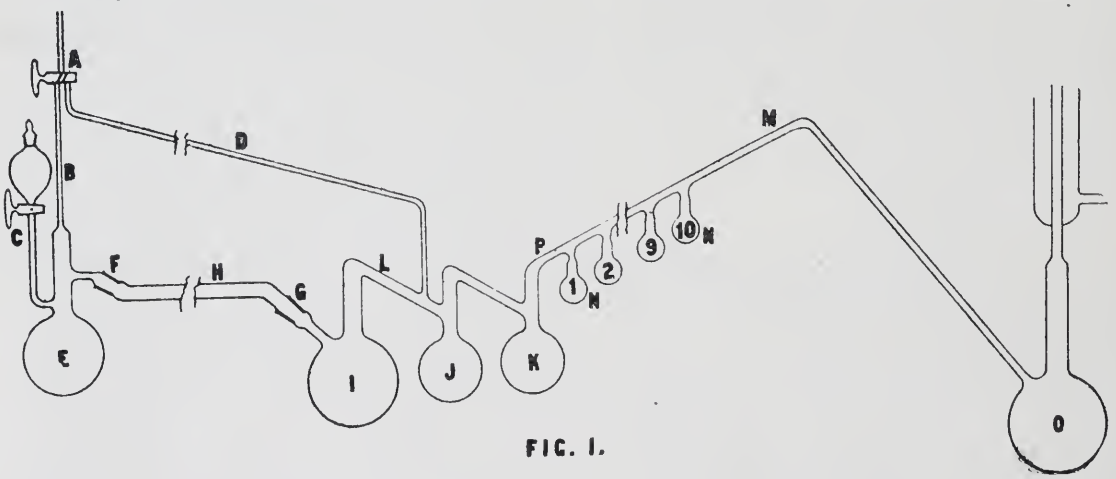


FIG. 1.

was then turned so as to deliver chlorine through D. The tantalum chloride was heated to boiling, and the entire apparatus heated, so that the residue of sulphur monochloride and some of the tantalum chloride was driven over into O. The entire amount of chloride was then distilled over into K, and finally into the small bulbs N. The chloride in all the bulbs was then brought to the boiling-point, and a small amount distilled over into the receiver O to insure the removal of the last traces of sulphur monochloride. When cold the apparatus was sealed off at P and M, and finally the individual bulbs were sealed off. These contained from 5 to 20 grms. of chloride.

The tantalum chloride so prepared was absolutely white in colour, having none of the pale yellow tint which this compound is usually said to possess. When fused the chloride had a pale straw-yellow colour. Five grms. of this chloride were thrown into a flask containing bromine water, and the contents heated for several hours. The tantalum hydroxide was filtered out, and the filtrate was evaporated to a very small bulk. This remained perfectly clear after the addition of a solution of barium chloride, which was taken to indicate that no sulphur remained in the preparation.

Density of Tantalum Chloride.—The density of this chloride was determined in carbon tetrachloride, and the number 3·62 obtained. Tantalum chloride is somewhat soluble in carbon tetrachloride, and consequently a more satisfactory determination was obtained when heptane was used. This liquid did not react with the chloride, nor did any of the the latter dissolve. The following results were obtained:—

Weight of pycnometer		10·2313
,, ,,	+ $TaCl_5$	23·6545
,, ,,	+ H_2O	35·2073
,, ,,	+ heptane	28·4050
,, ,,	+ heptane + $TaCl_5$ ..	39·1710

$t = 27°$. Density of $TaCl_5 = 3·68$

Density of Tantalum Oxide.—As was found in the case of columbium oxide, the density of the tantalum oxide obtained from the present determinations varied quite appreciably, the numbers 8·62, 7·91, and 8·06 having been obtained. The density of this substance is not far from that of the weights used, which were taken as having a density of 8·4, and it was found unnecessary to make a vacuum correction in the case of this substance.

Analysis of Tantalum Chloride.

The ratio studied was that of tantalum chloride to tantalum oxide, the transformation being made in quartz bulbs provided with tightly ground stoppers of quartz or glass. One of Ruprecht's best balances was used in the work, and the weights were carefully standardised. All weighings were made by substitution, using a tare of the same material and very nearly the same weight as the object being weighed. The excess weight of the quartz bulb and its stopper over the tare was determined. By carefully tapping one of the small bulbs containing the tantalum chloride the latter was broken up into small pieces, and by means of a file and a hot rod a crack was drawn about two-thirds of the way around the neck of the bulb. This bulb, together with the weighed quartz bulb, into the neck of which had been slipped a wide-neck funnel tube, were introduced into a gas-tight box supplied with a removable plate-glass top. Two holes had been cut in the sides of the box, and rubber gloves were attached on the inside. This box contained a large amount of calcium chloride, and a stream of air, which had been passed through large amounts of sulphuric acid, and then filtered through glass-wool, was passed through the apparatus for several hours. By slipping the hands into the gloves it was possible to remove the top of the bulb containing the chloride, and introduce the latter into the quartz bulb without soiling the neck of the bulb. In this way it was possible to effect the only transfer of material involved in the determinations in an atmosphere of dry air. After replacing the stopper in the quartz bulb the latter was removed from the box, and the excess of weight over the

tare again determined. The bulb was next placed in a vacuum desiccator containing water, and the air pumped out. In one or two days the chloride had completely hydrolysed, and the greater part of the hydrochloric acid produced had dissolved in the water outside of the bulb. A small amount of water and a few cc. of concentrated nitric acid were introduced into the bulb, and the mass evaporated to dryness with the aid of the apparatus shown in Fig. 2. The hood B was fastened to the neck of the bulb by means of the split rubber stopper E, which was prevented from actual contact with the neck of the bulb by means of a strip of filter-paper. F was a double-walled steam-bath. D contained cotton to filter the air which was drawn slowly through the apparatus by means of a water-pump attached at C. The mass was evaporated to dryness three times, a little water, and a small amount of nitric acid being added

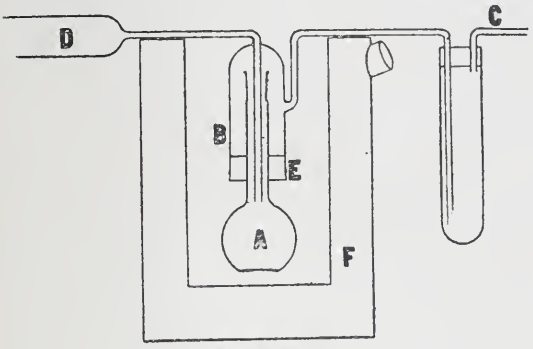


FIG. II.

each time. This insured the removal of the hydrochloric acid before the final ignition, which was made with a good blast-lamp arranged so that both the air and gas were filtered through cotton in order to minimise the amount of dust which might be blown against and adhere to the sides of the bulb. These ignitions were continued until no further loss of weight was observed. In making the calculations the atomic weight of chlorine was assumed to be 35·46. The temperature of the balance and the barometric reading were recorded in the case of the individual weights, and these numbers were used in applying the vacuum corrections. In the calculation the density of tantalum chloride was taken as 3·68 and that of the weights as 8·4. As mentioned previously, no vacuum correction was applied in the case of the tantalum oxide, since this correction, which was smaller than the error in weighing, affected the fifth decimal only. The following table includes the results of all determinations made which were carried to completion without accident: –

Series.	Bulb.	Wt of $TaCl_5$ (vac.).	Wt. of Ta_2O_5 (vac.).	100 parts of $TaCl_5$=parts of Ta_2O_5.	At. wt. of Ta.
II.	3	12·99680	8·02326	61·733	181·49
II.	5	9·24957	5·71104	61·744	181·60
II.	4	10·17456	6·28133	61·736	181·52
II.	1	17·99542	11·11014	61·739	181·55
II.	2	11·70558	7·22693	61·739	181·55
III.	4	6·24767	3·85658	61·728	181·46
III.	3	7·26375	4·48398	61·731	181·48
I.	2	15·88270	9·80465	61·732	181·49
				Mean	181·52

Summary.

In eight experiments 91·51605 grms. of tantalum chloride gave 56·49791 grms. of tantalum oxide, corresponding in round numbers to 181·5 as the atomic weight of tantalum, a number one-half a unit higher than that now given in the International Table. In conclusion, it may be as well to state that further work upon the value of this constant is in progress.

REPORT ON GASEOUS COMBUSTION.*

By WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S.

(Continued from p. 286).

Section IV.—*The Influence of Moisture upon Combustion.*

Thirty years ago H. B. Dixon, in repeating Bunsen's experiments on the division of oxygen between carbon monoxide and hydrogen, both present in excess, discovered that a mixture of carbon monoxide and oxygen, dried by long contact with phosphoric anhydride, will not explode when sparked in the usual way in a eudiometer, whereas the presence of a trace of moisture or of any gas containing hydrogen (*e.g.*, methane, ammonia, or hydrogen chloride) at once renders the mixture explosive. These experiments, proving as they did the complexity of what at first sight would appear to be one of the simplest cases of combustion, opened up a new field of scientific investigation.

In 1883 H. B. Baker, working in Dixon's laboratory at Balliol College, Oxford, found that purified charcoal, when heated to redness in carefully dried oxygen, burns with extreme slowness and without flame, yielding principally the monoxide, the proportion of the dioxide formed varying inversely with the degree of dryness of the oxygen. In a further series of experiments he proved that highly purified sulphur or phosphorus may be repeatedly distilled in an apparatus filled with carefully dried oxygen, without any combustion whatever occurring, although the admission of even a trace of moisture at once causes a vivid burning. In subsequent investigations extending over a number of years, Baker has shown that a large number of gaseous interactions are either conditioned or greatly accelerated by the presence of moisture. Thus a dried mixture of hydrogen and chlorine does not explode on exposure to sunlight, dried ammonia and hydrogen chloride are mutually inert, and dried electrolytic gas, free from hydrocarbon impurity, can be heated to redness without exploding.

The amount of moisture required to bring about such chemical changes as the above is surprisingly small. E. W. Morley has estimated that the mere passing of a gas through a long column of phosphoric anhydride leaves only 3 mgrms. of water-vapour in a million litres (or rather less than 4 molecules of steam per 1000 million molecules of gas), and yet a much more prolonged drying is usually required to inhibit chemical action. Such facts as these, even if they do not raise doubts as to the adequacy of the usually accepted kinetic views of chemical processes, at least suggest the necessity of some less stringent application of them.

The dependence of the combustion of carbon monoxide upon the presence of water-vapour is well illustrated by H. B. Dixon's determination of the rates of explosion for mixtures of carbon monoxide and oxygen in combining proportions containing varying amounts of water-vapour. Starting with a "well-dried" mixture, the rate of explosion increases with successive additions of moisture, from 1264 to a maximum of 1738 metres per second for a mixture saturated at 35°, any further addition of steam having a decidedly retarding influence, as follows :—

Rates of Explosion, at 10° and 760 mm., for a Mixture $2CO + O_2$ *containing varying Proportions of Steam.*

Hygroscopic condition.	Per cent moisture.	Rate in metres per second.
Well dried	—	1264
Saturated at 10°	1·2	1676
,, 20°	2·3	1703
,, 28°	3·7	1713
,, 35°	5·6	1738
,, 45°	9·5	1693
,, 55°	15·5	1666
,, 65°	24·6	1526
,, 75°	38·0	1266

* Read before the British Association (Section B), Sheffield Meeting, 1910.

Before entering upon a discussion of the theoretical aspects of the matter, certain other facts must be considered, namely:—

1. In the detonation of a dried mixture of cyanogen with twice its own volume of oxygen the formation of carbon dioxide is complete; moreover, under such conditions it has been proved that carbon monoxide is primarily formed in the wave itself, the second stage of the combustion—namely, $2CO + O_2 = 2CO_2$—taking place in the rear of the wave (H. B. Dixon).

2. A well-dried mixture of carbon monoxide (36 per cent), ozone (8 per cent), and oxygen cannot be fired with a powerful electric spark; also, on sparking a well-dried mixture of carbon monoxide (60 per cent), chlorine peroxide (29 per cent), and oxygen (11 per cent), although a flame is propagated through the gases, as much as 76 per cent of the original carbon monoxide may remain unburnt H. B. Dixon and E. J Russell, *Trans. Chem. Soc.*, 1897, xxi., 605).

3. Dried carbon monoxide and oxygen completely combine without flame in contact with a heated platinum wire; moreover, the writer has recently proved that the most careful drying possible greatly accelerates the rate at which the gases combine in contact with a hot fire-clay surface at 500°.

4. There are certain well-established instances in which combustion is not determined by the presence of moisture—namely, the combustion of cyanogen, of carbon disulphide, and of hydrocarbons (ethane, ethylene, and acetylene).

Theories Respecting the Function of Moisture.

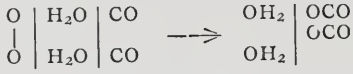
1. H. B. Dixon has consistently maintained that, in the combustion of carbon monoxide, steam merely acts as the carrier of oxygen; he contends that in explosions the formation of carbon dioxide is always limited by its dissociation, and that at the highest temperature (*e.g.*, in the wave-front when the mixture $C_2N_2 + 2O_2$ is detonated) it is not formed at all by *direct* interaction of the monoxide and oxygen, because the internal energy which would thereby be imparted momentarily to the newly-born dioxide molecule would bring about its dissociation. For the same reason flame is not propagated through a dried mixture of carbon monoxide and oxygen. But, if steam be present, the interaction of $CO + OH_2 = CO_2 + H_2$ would bring molecules of the dioxide into existence with a much less degree of internal agitation, and therefore capable of continued existence, whilst the hydrogen liberated would immediately combine with oxygen, forming steam, which is less easily dissociated than carbon dioxide. This explanation, whilst consistent with many of the facts connected with the combustion of carbon monoxide, cannot be extended to other well-known instances, and is particularly inapplicable to the case of hydrogen.

2. Mendeleeff, in his "Principles of Chemistry," ascribed the mutual inertness of carbon monoxide and oxygen to the circumstance that gases combine according to a supposed "*law of equal volumes*," or, in other words, that from the kinetic standpoint the primary changes in all cases must be considered as involving the collision of two molecules only. In the case of carbon monoxide he postulated the following cycle of changes:—

(i.) $CO + OH_2 = CO_2 + H_2$; (ii.) $H_2 + O_2 = H_2O_2$;
(iii.) $CO + O_2H_2 = CO_2 + OH_2$.

But, according to this supposed "*law of equal volumes*," a well-dried mixture of carbon monoxide and nitrous oxide, or of carbon monoxide and ozone, should be active, whereas Dixon has proved them to be as non-explosive as a dried mixture of the monoxide and oxygen.

3. H. E. Armstrong has always contended that chemical actions cannot occur between two perfectly pure substances, but require the conjunction of an electrolyte in order to form a closed conducting system. The presence of steam, which he supposes may always be regarded as rendered "conducting" by association with some traces of an electrolyte impurity, provides the necessary conditions for the passage of the current, the oxygen playing the part of depolariser, thus:—



On the other hand, H. B. Dixon has urged that a rate of explosion of nearly 1700 metres per second for a moist mixture of carbon monoxide and oxygen is incompatible with any interaction of the complexity thus postulated. There is doubtless *prima facie* much force in this objection, but it is by no means fatal, seeing that the dimensions of the explosion wave are incomparably greater than molecular units, and the duration of chemical action, though extremely short when measured in terms of ordinary gross units of time, is at least many thousands of times greater than the intervals between successive molecular collisions (see Note). A more serious objection to Armstrong's theory is the fact that there are several well-established cases in which combustion apparently does not depend upon the presence of moisture.

(Note.—As the writer understands Dixon's objection to Armstrong's view, it is that whilst chemical action in the explosion wave may *last* a comparatively long time (*i.e.*, during many molecular collisions), and that therefore a quintuple molecular collision might happen in that period, it is impossible for the wave to be *propagated* as a sound-wave through quintuple collisions. Ordinary sound-waves may be many molecules *thick*, but they are propagated through bi-molecular collisions).

4. In 1893 Sir J. J. Thomson (*Phil. Mag.*, xxxvi., 321) pointed out that if the forces holding the atoms together in a molecule are electrical in character, the presence of drops of any liquid (such as water) of high specific inductive capacity would probably cause a sufficient loosening of the bands between the atoms to render the molecule much more reactive. He showed that the complete drying of a gas renders it non-conductive. H. B. Baker, in his Wilde Lecture before the Manchester Literary and Philosophical Society (*Man. Mem.*, liii., part 3), described a number of new experiments which led him to tentatively put forward the theory that chemical interchanges in gaseous systems depend upon the presence of both "ions" and water-vapour; the "ions" act as nuclei for the condensation of steam, and the liquid drops of water so formed, by virtue of their high specific inductive capacity, facilitate chemical change in the layer of gas immediately in contact with them. Chemists will await with the greatest interest the further development of this hypothesis, but the idea that such rapid changes are met with in gaseous explosions are dependent upon the formation of *aggregates* of steam molecules in an atmosphere containing less than four of them per 1000 millions, and that such aggregates approximate to *liquid drops* at the high temperatures of flames, makes large demands upon the imagination, and it will require to be supported by the strongest experimental evidence.

(To be continued).

Behaviour of Iron towards Solutions of Stannous Salts.—A. Thiel and K. Keller.—The authors have performed a series of experiments to discover whether iron actually precipitates tin from solutions of stannous salts. These experiments included both determinations of the rate of the reaction between iron and an acid solution of a tin salt, and also determinations of electromotive force, and in both cases it was found that tin is separated when iron is immersed in a solution which is not too acid and not too poor in tin. The same result was obtained analytically, and thus tin and iron behave as would be expected from their position in the tension series.—*Zeit. Anorg. Chem.*, lxviii., No. 3.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 24th, 1910.

Sir Archibald Geikie, K.C.B., President, followed by Mr. A. B. Kempe, Vice-President, in the Chair.

Papers were read as follows:—

"*Sequence of Chemical Forms in Stellar Spectra.*" By Sir Norman Lockyer, K.C.B., F.R.S.

This paper gives in the first place a *résumé* of the facts obtained from a study of various celestial and laboratory spectra from 1873 to 1905, in so far as they relate to the working hypothesis formulated in 1873, that in the reversing layers of the sun and stars various degrees of celestial dissociation are at work.

It is shown that each step in the study of celestial and laboratory spectra and their inter-relation has strengthened that hypothesis, and that it has enabled a classification of stars—based on their chemistry and heat conditions—to be made.

This classification has been recently checked by studying the physical conditions of stars, using a calcite-quartz optical train to obtain photographs of the extension of the spectra of each chemical group of stars into the ultra-violet on the same plate and under equal conditions of atmosphere and altitude. This confirmed the prior chemical results, absolute parallelism being found between the two sets of photographs.

The recent researches detailed in the paper have been made with better photographs and with increased knowledge of the changes in spectra. This work has enabled the classification to be carried into finer details, and the heat levels at which various chemical forms are predominant have been observed with greater certainty. Thus the Alnitamian group of stars in the Kensington classification has been divided into four species. These indicate the effects of four different temperatures, associated with observed changes in spectral lines. When in the laboratory special groups of lines appear at different temperatures, each group is predominant in turn in stars of different temperatures. In the laboratory the effects of all temperatures are integrated; in stars the low temperature and therefore its effects are absent.

Diagrams are given (1) showing the range through stars of rising temperature of the different chemical forms, and also stellar level at which each chemical form predominates; (2) relation of the four sub-divisions of the Alnitamian group to groups immediately above and below it on stellar temperature curve.

The chemical forms predominant in spectra of hottest stars are hydrogen, photohydrogen, silicium, carbon, nitrogen, oxygen, sulphur, and the cleveite gases. These researches into the finer details of stellar and laboratory spectra have afforded help in dealing with stars showing peculiar spectra. It has been shown that ε Ursæ Majoris, a Sirian star with peculiarities, has the lines of protochromium more developed than any other star yet examined, either higher or lower on the stellar temperature scale. Other stars with peculiar spectra have been found to have sets of lines which have not yet been traced in terrestrial spectra.

"*Influence of Viscosity on the Stability of the Flow of Fluids.*" By A. Mallock, F.R.S.

The effect of this paper is to call attention to an observation made by the late Mr. W. Froude, F.R.S., with regard to an experiment on fluid jets, and to its application in explaining some of the phenomena presented by the flow of viscous fluids.

The experiment referred to was shown by Froude at the Bristol Meeting of the British Association in 1875, and one of the deductions drawn from it was that in a viscous flow the character of the stream differed according as to whether the flow was towards decreasing or increasing pressure.

"*Atmospheric Oscillations.*" By Horace Lamb, F.R.S.

The paper treats of the free oscillations of an atmosphere, the temperature being a function of the altitude, and the adiabatic laws of expansion being assumed. In particular the case of a uniform temperature gradient is discussed in some detail. The possible oscillations are of various types, of which the most important is of the character of a longitudinal wave. The results are simplest when the equilibrium state is one of convective equilibrium, and the velocity of the longitudinal wave is then equal to the Newtonian velocity of sound, $\sqrt{(gH)}$, corresponding to the temperature of the lowest stratum. The bearing of the results on Kelvin's theory of the semidiurnal barometric oscillation is examined; and it appears that the existence of a free period of the earth's atmosphere, of somewhat less than twelve mean solar hours, is highly probable. Other types of oscillation depend for their frequency on the degree of stability of the atmosphere, and may under circumstances be comparatively slow. It is possible that these may account for some of the minor fluctuations of the barometer. The paper includes also an examination of the theory of waves at a surface of discontinuity.

"*A Theory of the Chemical Action of the Electric Discharge in Electrolytic Gas and other Gases.*" By P. J. Kirkby.

The complicated results attending the passage of an electric discharge through electrolytic gas, described in previous papers, and in particular the chemical effects observed in the positive columns of long discharges, were explained by the theory that the chemical action is due to molecular dissociation effected by the collisions of gaseous ions constituting the current with the molecules of the gas, the atoms of which are thus set free to enter into new combinations.

In this paper an account is given of experiments designed to determine both the number of molecules of water (w) formed by the passage of the atomic charge through 1 cm. of the positive columns of various discharges passed through electrolytic gas ($2H_2+O_2$), and also the electric force (Y) within these columns—the results providing data for testing and developing the theory. The chemical effects of the positive column are attributed to the motion of the electrons alone. The number of atoms of oxygen set free by the collisions of an electron moving through 1 cm. in electrolytic gas at p mm. pressure under the electric force Y is of the form $cpe^{-bp/Y}$ where c, b are certain constants. Hence, if an atom of oxygen can unite directly with a *molecule* of hydrogen w is proportional to $cpe^{-bp/Y}$. All the experimental results satisfy this condition within error-limits in the particular form $w/p = 7{\cdot}9\,e^{-42{\cdot}7\,p/Y}$, and thus support the above theory as well as the hypothesis that water-vapour is formed by the collision of an atom of oxygen with a molecule of hydrogen.

This equation involves that the energy of formation of an oxygen-molecule is less than, and probably nearly equal to, $6{\cdot}1\times10^{-12}$ ergs; and experiments of Berthelot upon the heat of transformation of ozone into oxygen are shown to be in fair agreement. An estimate, 7×10^{-12} ergs, is also given for the energy of formation of a molecule of water-vapour.

These experiments also prove, independently of theory, that dissociated atoms of oxygen are not charged electrically.

Similar experiments were made with the gaseous mixture $CO+H_2$. The chemical effects observed in the positive column reproduce the main features observed with electrolytic gas, and are explainable by a similar theory.

"*Electrostatic Voltmeter for Photographic Recording of the Atmospheric Potential.*" By G. W. WALKER.

The paper describes some experiments made at Eskdalemuir observatory, with the object of obtaining a simple and efficient voltmeter for continuous photographic registration of the electrical potential at a fixed point in the atmosphere. Experience has shown that occasionally the instrument would require to register up to fully 1000 volts + or −.

Satisfactory results have been obtained by means of a Dolezalek electrometer. The usual sensitiveness was greatly reduced by using a phosphor-bronze suspension, while the needle was loaded to prevent tilting. A fixed difference of potential is applied between the quadrants by means of one or two standard cadmium cells, while the potential to be measured is applied to the needle. The needle can now carry 1100 volts with perfect safety and stability, while the scale value on the paper is constant to within a few per cent over a range from − 900 to + 900 volts.

Trial has been made of a voltmeter (made in the workshop), similar in general design to the Dolezalek, but in which the fixed difference of potential between the quadrants is provided by making the quadrants alternately of copper and zinc soldered together and not insulated. Uniformity of scale value has been obtained from about − 500 to + 500 volts, but for higher potentials only approximate uniformity was secured. This defect arises from want of mechanical perfection of the quadrants and needle, and should disappear in an instrument made with the same accuracy as the Dolezalek. At present, also, the damping of the needle during very rapid changes of potential is insufficient.

Reference is made to certain points in the manipulation of sulphur for insulating, which have been found essential to secure good results.

"*Optical Dispersion: An Analysis of its Actual Dependence upon Physical Conditions.*" By T. H. HAVELOCK, M.A., D.Sc.

The paper is based upon a generalised dispersion formula—

$$\frac{1}{\sigma + 1/(n^2 - 1)} \cdot \frac{1}{P} = \Sigma \frac{c_s}{\lambda^2 - \lambda^2_s} ;$$

where P is the density of the medium. The quantities c_s and λ_s refer to natural vibrations inherent in the molecule, and it is assumed that these are not changed by varying physical conditions, such as temperature, pressure, or density; thus an attempt is made to express these conditions in their optical effect by two variables P and σ.

The scheme is tested first by a relation deduced from the above formula, namely, the difference in value of $P/(n^2 - 1)$ for any two physical conditions of the same substance is constant in regard to wave-length. From an examination of available data this appears to be satisfied approximately for gases and liquids, and for changes from gas to liquid. Numerical values of σ for various substances in different conditions are obtained by assigning it zero value for the gaseous condition at normal pressure and temperature.

Artificial double refraction is included in the same formal scheme by allowing anisotropic changes of the quantity σ.

Finally for dispersion formulæ of the above type, an observed maximum of absorption (or of selective reflection) is identified, not with λ_s, but with a wave-length λ'_s, differing from λ_s by a term involving P and σ; numerical examples are given for rock salt and fluorite. The wave-lengths λ'_s are calculated under various conditions for certain substances; experimental data are analysed to show the pressure-displacement for air and the temperature-displacement of absorption maxima for water and carbon disulphide.

"*Spectrum of Halley's Comet.*" By C. P. BUTLER.

Provision was made for photographing the comet and its spectrum from the beginning of May, 1910, at Foster-down, Caterham. Exceptionally bad weather prevented observations until the end of the month, when photographs and visual observations of the spectrum were obtained on May 23 and 26.

The photographs of the comet taken with a Dallmeyer lens, 6 inches aperture, 50 inches focus, show that the nucleus was at times multiple. Visual observations of the nucleus showed strong continuous spectrum with three bands in the yellow-green, green, and greenish-blue, having approximate wave-lengths 5635 (int. 7), 5165 (int. 10), 4737 (int. 7).

The spectrum of the coma surrounding the nucleus consisted of these same three bands, without any indication of continuous radiation. The photographic spectra show only the brightest features of the spectrum of the nucleus, the relative intensities differing widely from the visual intensities owing to the selective sensitiveness of the plates. The two most conspicuous bands are near λ 4737 (int. 10), and 3884 (int. 6), with fainter bands near λλ 4050, 4360, 5165, and 5635.

Photographs obtained elsewhere at different times show differences in the relative intensities of the component bands. This has been ascribed to variations of atmospheric absorption. It may be noted, however, that before and after the transit on May 19 the aspect of the head would vary quickly; at one time the hotter side facing the sun would be best seen; at others, the cooler portions away from the sun would be more prominent. Preliminary experiments show that by varying conditions of vaporisation the relative intensities of the carbon or hydrocarbon bands may be considerably modified, and it would appear that the changes observed in the cometary spectrum might be produced by some such difference of condition.

"*Geometrical Proof of the Theorem of a Double Six of Straight Lines.*" By Dr. H. F. BAKER, F.R.S.

CHEMICAL SOCIETY,

Ordinary Meeting, November 3rd, 1910.

Prof. HAROLD B. DIXON, M.A., Ph.D., F.R.S., President, in the Chair.

(Concluded from p. 292).

*281. "*The Constituents of Gelsemium.*" By CHARLES WATSON MOORE.

The material employed in this investigation consisted of the dried rhizome and roots of *Gelseminm sempervirens*, Aiton.

An alcoholic extract of the drug, when distilled in a current of steam, yielded a small quantity of an essential oil. The non-volatile constituents of the extract consisted of a brown resin insoluble in water, and material which remained dissolved in the cold aqueous liquid. The resin, which amounted to about 3·8 per cent of the weight of the drug, yielded pentatriacontane; traces of emodin monomethyl ether; a phytosterol, $C_{27}H_{46}O$ (m. p. 136°; $[\alpha]_D$ −40·4°); a small amount of ipuranol, $C_{23}H_{38}O_2(OH)_2$; and a mixture of palmitic, stearic, oleic, and linolic acids. The portion of the alcoholic extract of the drug which was soluble in water contained scopoletin (a monomethyl ether of æsculetin), which was present in the free state, and also in the form of a glucoside, together with a quantity of sugar. It yielded, furthermore, three alkaloidal products, one of which, gelsemine, has been obtained in a pure crystalline state, melting considerably higher than has hitherto been recorded (178° instead of 160°), and which has been shown to possess the formula $C_{20}H_{22}O_2N_2$. The other alkaloidal products, one of which corresponds with the so-called "gelseminine" of Thompson (*Jahresber.*, 1887, p. 2218) and Cushny (*Ber.*, 1893, xxvi., 1725), were amorphous, and no crystalline derivatives could be obtained from them.

282. "*Some Phenolic Derivatives of β-Phenylethylamine.*" By GEORGE BARGER and ARTHUR JAMES EWINS.

In order to examine the relationship between physiological activity and chemical constitution the authors have prepared a number of bases related to and intermediate between *p*-hydroxyphenylethylamine and α-3 : 4-trihydroxy-β-phenylethylmethylamine (adrenaline), the two latter bases being chemically and physiologically similar. The following bases were described :—*4-Hydroxy-3-m-tolylethylamine*, $OH \cdot C_7H_6 \cdot CH_2 \cdot CH_2 \cdot NH_2$; *3 : 4-dihydroxy-β-phenylethylamine*, $C_6H_3(OH)_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$; *2 : 3 : 4-trihydroxy-β-phenylethylamine*, $C_6H_2(OH)_3 \cdot CH_2 \cdot CH_2 \cdot NH_2$; and *ω-amino-2 : 3 : 4-trihydroxyacetophenone*, $C_6H_2(OH)_3 \cdot CO \cdot CH_2 \cdot NH_2$.

A number of intermediate products employed in the syntheses were also described.

283. "*Chloroamine Reactions: Methylenechloroamine.*" By Charles Frederick Cross, Edward John Bevan, and William Bacon.

The authors have extended the observations of Raschig (*Ber.*, 1907, xl., 4586) on monochloroamine, and have characterised the products of reaction of gelatin and various proteins with chlorine as chloroamine derivatives.

Methylenechloroamine, $CH_2{:}NCl$, is prepared by the interaction of monochloroamine and formaldehyde according to the equation $NH_2Cl + CH_2O = CH_2{:}NCl + H_2O$. The compound is readily obtained from hypochlorites (N/2-solution) by adding ammonium chloride and formaldehyde at the ordinary temperature. It crystallises from chloroform in large needles.

(The name methylenechloroamine is retained pending the final settlement of the constitution of the compound in order to indicate its relation to chloroamine).

284. "*The Formation and Reactions of Imino-compounds.* Part XIV. *The Formation of α-Hydrindone and its Derivatives.*" By Alec Duncan Mitchell and Jocelyn Field Thorpe.

It was shown that the compound prepared by Gabriel and Hausmann by the action of ethyl sodiomalonate on *o*-cyanobenzyl chloride, and described by them as ethyl *o*-cyano-β-phenylpropionate (I.), is in reality ethyl 1-iminohydrindene-2-carboxylate (II.), and that it is converted by hydrochloric acid into ethyl 1-hydrindone-2-carboxylate (III.).

$C_6H_4{<}^{CN}_{CH_2 \cdot CH_2 \cdot CO_2Et}$ I. $\qquad C_6H_4{<}^{C(:NH)}_{CH_2 \text{—}}{>}CH \cdot CO_2Et$ II.

$C_6H_4{<}^{CO\text{—}}_{CH_2}{>}CH \cdot CO_2Et$ III.

It was also shown that under suitable conditions the normal product of this condensation, namely, ethyl cyanobenzylmalonate, $CN \cdot C_6H_4 \cdot CH_2 \cdot CH(CO_2Et)_2$, can be prepared, and that on treatment with a small quantity of alcoholic sodium ethoxide it passes at once into ethyl carbonate and ethyl 1-iminohydrindene-2-carboxylate. In the same way the normal product of the condensation of ethyl sodioacetoacetate with *o*-cyanobenzyl chloride, namely, ethyl *o*-cyano-α-benzylacetoacetate,—

$$CN \cdot C_6H_4 \cdot CH_2 \cdot CH(COMe) \cdot CO_2Et,$$

passes into ethyl acetate and ethyl 1-iminohydrindene-2-carboxylate, and when the sodium compound of ethyl cyanoacetate is used, the normal product, namely, ethyl α-*o*-dicyano-β-phenylpropionate, $CN \cdot C_6H_4 \cdot CH_2 \cdot CH(CN) \cdot CO_2Et$, passes under the same treatment into 1-imino-2-cyanohydrindene and ethyl carbonate. The products derived from these imino-compounds and from the corresponding ketones were described.

285. "*Experiments on the Synthesis of the Terpenes.* Part XIV. *Synthesis of* d- *and* l-Δ^5-m-*Menthenol*(8), dl-Δ^4-m-*Menthenol*(8), *and their Derivatives.*" By William Henry Perkin, jun.

The author described the conversion of 1-methyl*cyclo*hexan-3-ol-5-carboxylic acid (*Trans.*, 1909, xcv., 1889) into methyl-Δ^5- and 1 methyl-Δ^4-*cyclo*hexen-3-carboxylic acids, the resolution of the former into its active modifications, and the synthesis, with the aid or these acids, of the menthenols and menthadienes mentioned in the title.

286. "*Experiments on the Synthesis of the Terpenes.* Part XV. Δ^3-m-*Menthenol*(8) *and* $\Delta 3 : 8(9)$-m-*Menthadiene.*" By Bernard Dunstan Wilkinson Luff and William Henry Perkin, jun.

The authors have discovered a new method by which 1 methyl-Δ^3*cyclo*hexen-3-carboxylic acid may be prepared in quantity and converted into Δ^3-*m*-menthenol(8) and $\Delta 3 : 8(9)$-*m*-menthadiene. The physical properties of these substances were discussed in detail.

287. "*The Morphotropic Relationships between Silicon and Carbon Compounds of Corresponding Compositions.*" By Georg Jerusalem.

The suggestion made by Barlow and Pope as a result of their work on crystal structure, that carbon is the only element which is fundamentally quadrivalent, and that silicon and the other elements of group IV. exhibit a fundamental valency of two, finds support in the fact that no properly authenticated case is known in which carbon and silicon are isomorphously replaceable. It is remarked that corresponding carbon and silicon compounds of high molecular symmetry and great molecular complexity might be expected to exhibit isomorphous or morphotropic relationships in spite of the difference in fundamental valency between the two elements. The author has determined the crystalline forms of tribenzylcarbinol, tribenzylmethyl chloride, tribenzylsilicol, triphenylcarbinol, and triphenylsilicol, and shows that a very close morphotropic relationship holds between the first three compounds; this furnishes the first recorded case of morphotropy between corresponding carbon and silicon compounds. It was further shown that the crystallographic data, just as is the case in the humite series of minerals, accord rather better with the view that the fundamental valencies of carbon and silicon are in the ratio of 4 to 2 than with that in which the same fundamental valency of 4 is assigned to both elements.

288. "*The Resolution of Externally Compensated Pavine and α-Bromocamphor-π-sulphonic Acid.*" By William Jackson Pope and Charles Stanley Gibson.

A convenient method was described for preparing the dihydropapaverine, pavine, and a process was detailed for resolving it quantitatively into its optically active components by the use of *d*- and *l*-α-bromocamphor-π-sulphonic acid. The optically active pavines can be used in effecting the resolution of externally compensated α-bromocamphor-π-sulphonic acid.

289. "*The Rotatory Powers of the Salts of* d- *and* l-*Camphor-β-sulphonic Acid with* d- *and* l-*Pavine.*" By William Jackson Pope and Charles Stanley Gibson.

The salts of *d*- and *l*-pavine with *d*- and *l*-camphor-β-sulphonic acid have been prepared, and determinations made of the rotatory powers of these four salts for light of three different wave-lengths. The molecular rotatory powers of the basic and acidic ions can be calculated roughly from the observed values obtained from the above salts in dilute aqueous solution, but the discrepancies are too large to be attributed to experimental error.

290. "*Externally Compensated Tetrahydroquinaldine* (2-*Methyltetrahydroquinoline*) *and its Optically Active Components.*" By William Jackson Pope and John Read.

Externally compensated tetrahydroquinaldine (2 methyltetrahydroquinoline) crystallises when its solution in light petroleum is cooled in liquid air, and on inoculating the pure substance at the ordinary temperature with the solid thus obtained, crystallisation occurs. A method was described for quantitatively resolving the base into its optically active components by the aid of *d*- and *l*-α-bromocamphor-π-sulphonic acid.

291. "*The Distillation of Mixtures of Enantimorphously Related Substances.*" By William Charles Evans.

The mode in which a number of optically active mixtures of *d*- and *l*-camphor and of *d*- and *l*-2-methyltetrahydroquinoline behave on distillation under varying conditions has been studied. It was shown that in these cases the mixtures behave like single substances on distillation, and that no separation of the components can be effected by distillation under ordinary or diminished pressures.

292. "*The Tertiary Acidic and Alkyl Derivatives of* d-*Camphorimide.*" By William Charles Evans.

For the purpose of investigating the similarity of behaviour of phthalimide and *d*-camphorimide, a number of acidic and alkyl derivatives of the latter have been prepared by methods applicable to the former imide. The sodio-derivative of *d*-camphorimide, the corresponding bromo- and iodo-imides, and the tertiary alkyl compounds in which the iminic hydrogen atom of *d*-camphorimide is replaced by methyl, ethyl, benzyl, and *p*-nitrobenzyl, have been prepared and examined polarimetrically.

293. "*The Relation between the Crystal Structure and the Chemical Composition, Constitution, and Configuration of Organic Substances.*" By William Barlow and William Jackson Pope.

The authors have extended their previous work on this subject, and have applied the methods previously used to the study more particularly of the paraffins, olefines, and acetylenic hydrocarbons. Thus, homogeneous close-packed assemblages have been constructed of spheres of atomic influence of two kinds, representing carbon and hydrogen and of the volume ratio, 4 : 1, present in the numerical proportions indicated by the general composition, C_nH_{2n+2}, of the paraffins; it is found that such an assemblage can be devised to correspond in composition with any paraffin, and that the geometrical partitioning of the assemblage yields a molecular unit in close accord with the generally accepted space configuration of the paraffins. Assemblages have also been constructed corresponding with the olefine and acetylenic hydrocarbons, and these exhibit geometrical features, which, it is claimed, represent the presence in the molecule of an ethylenic and acetylenic bond respectively. The relation existing between the acetylenic and aromatic hydrocarbons has also been examined in a similar manner.

It has also been shown that the geometrical results obtained are in accordance with the crystallographic data available for the halogen derivatives of the hydrocarbons.

294. "*Synthesis of* 1 : 1 : 3-*Trimethyl*cyclo*hexene* (cyclo*geraniolene*)." By Arthur William Crossley and Charles Gilling.

1 : 1 : 3-*Trimethyl*cyclo*hexan*-3-*ol* has been prepared by the action of magnesium methyl iodide on 1 : 1-dimethyl-*cyclo*hexan-3-one. The hydroxyl group of the alcohol is

$$CMe_2<\begin{matrix}CH_2\cdot CMe(OH)\\ CH_2\text{———}CH_2\end{matrix}>CH_2$$

readily displaced by bromine, and from the resulting bromide, potassium hydroxide eliminates the elements of hydrogen bromide with production of isomeric forms of 1 : 1 : 3-trimethyl*cyclo*hexene, which have been proved to be identical with *cyclo*geraniolene.

295. *The Viscosity and Density of Cæsium Nitrate Solutions.*" By Thomas Ralph Merton.

The densities and viscosities of solutions of cæsium nitrate in water have been determined at 0°, 10°, 18°, and 25° at concentrations varying from 0·02-N to saturation. The results are in agreement with the general principles discovered for other salt solutions. In the case of cæsium nitrate solutions the viscosity decreases with increasing concentration.

296. "*The Starch Iodine Reaction.*" By William Harrison.

The author finds that in the formation of the blue iodide of starch the presence of iodides is not necessary. The blue colour is formed with pure iodine, but the depth is increased by the presence of any salt or weak acid. The gradual addition of alcohol changes the blue to violet, red, orange, and yellow, and the reverse change takes place on dilution with water. The same colour-change is produced by carefully heating the blue solution, and the reverse phenomena are observed on cooling.

This colour-change is analagous to the colour-change of colloidal gold solution investigated by Zsigmondy, which changes from red to blue on adding salts.

The author succeeded in preparing a blue colloidal solution of iodine in water containing glycerol and no starch, but the colour only remained for a fraction of a second, the iodine being precipitated.

It was shown that all the iodine can be removed from starch iodide by washing with pure water, and the conclusion is drawn that the blue solution of iodine and starch, is a colloidal solution of iodine, the starch acting as a protective colloid. It was further shown that the reactions of dextrins and starch celluloses can be obtained with starch under certain conditions, from which the conclusion is drawn that dextrins and starch celluloses are all different colloidal states of starch, and not chemically different compounds.

297. "*Aromatic Hydroxy-sulphoxides.*" By Maud Gazdar and Samuel Smiles.

The hydroxy-derivatives of aromatic sulphoxides are attacked by concentrated sulphuric acid, furnishing substances which exhibit a deep blue colour in that medium. As a preliminary to the investigation of the reaction, the sulphoxides of *p*-cresol, *o*-, and *p*-chlorophenol and their derivatives have been examined.

298. "*Binary Mixtures of some Liquefied Gases.*" By Bertram Dillon Steele and L. S. Bagster.

The authors have examined the variation of vapour pressure with temperature and with composition for mixtures of sulphur dioxide and hydrogen bromide, hydrogen sulphide and hydrogen bromide, and hydrogen sulphide and hydrogen iodide. Curves have been drawn for total and partial pressures through a considerable temperature range, and also the pressure-composition curve of each pair at one temperature.

A specially constructed apparatus was employed, admitting of the removal of samples of both liquid and vapour for analysis.

The vapour pressure curve of mixtures of sulphur dioxide and hydrogen bromide is of a well-known type, and is such as might be expected from the properties of the ingredients. In the case of hydrogen sulphide and hydrogen bromide, the curves show that a mixture exists of minimum vapour pressure or maximum boiling-point. This is interesting in view of the fact that the solution is not an electrolytic conductor, and that neither ingredient forms associated molecules, whilst the hypothesis that the peculiarity is due to the formation of an additive compound is difficult to reconcile with the fact that hydrogen sulphide and hydrogen iodide give a different form of curve. This mixture affords a new instance of the somewhat rare phenomenon of an ideal binary mixture; that is, one to which Raoult's law applies over the whole range of concentration.

299. "*Lead Silicates in Relation to Pottery Manufacture.*" By Sir Edward Thorpe and Charles Simmonds.

The authors have carried out some experiments showing the direction in which certain constituents of lead silicates influence the resistance of the silicates to attack by dilute acids. Alumina makes the compounds more stable; sodium oxide has the opposite effect; boron trioxide decreases the resistance in some cases, but has no such influence in others. Attention was also drawn to a recent publication by Beck, Löwe, and Stegmüller dealing with the same subject.

PHYSICAL SOCIETY.

Ordinary Meeting, November 25th, 1910.

Prof. H. L. Callendar, F.R.S., President, in the Chair.

A paper entitled "*The Electric Stress at which Ionisation begins in Air*" was read by Dr. A. Russell.

In the *Proceedings of the American Institution of Electrical Engineers* for July, 1910, Prof. J. B. Whitehead publishes the values of the electric stress at which ionisation begins in air. The electrodes he used in his experiments consisted of a metal tube and a cylindrical wire coaxial with it. Alternating pressures were employed, and the inner wires used had diameters varying in size from 0·089 to 0·475 cm. If a be the radius of the inner wire, the author has found that the expression $32 + 13{\cdot}4\sqrt{a}$ gives all Whitehead's experimental results for the maximum electric stress in kilovolts per cm. with a maximum inaccuracy of less than 1 per cent. The experiments show that the electric stress at which ionisation occurs is independent of the metals used for the electrodes and of the inner radius of the outer tube. It depends merely on the radius of the inner wire. It is shown that Steinmetz's experimental results on the sparking distances between parallel rods are in substantial agreement with Whitehead's figures. Possible reasons for the discrepancies are given. An empirical formula is given which is based on experimental results recently published by Kowalski and Rappel for the sparking voltages between equal spherical electrodes. The results indicate that the electric stress at the moment of discharge has a minimum value when the distance between the electrodes is a certain function of their radius. The author lays great stress on the currents of electrified air which stream round the electrodes before the discharge takes place, and the effects of which it is customary to neglect. These currents often modify very appreciably the values obtained for the disruptive stress at the moment of discharge. The striking similarity between the formulæ for the temperature gradient at the surface of a hot wire cooling in air and the empirical formula for the potential gradient at the surface of an electrified wire when ionisation is taking place at its surface is pointed out.

Dr. C. Chree expressed his interest in the paper, and remarked that when the electrodes were close together electrostatic attraction might produce an actual transfer of matter from one electrode to the other. The effect of the electrostatic attraction on the diminution of the distance between the electrodes would depend upon the nature of the apparatus used.

Prof. Strutt remarked that the effects which the author had discussed in his paper might be attributed to causes similar to those suggested by Dr. Chree.

Mr. Erskine-Murray gave some particulars of Dr. Shaw's experiments on the subject, and asked the author if he would extend his researches to electrodeless discharges.

Mr. D. Owen expressed his interest in the paper, and pointed out that the experimental results depended upon the strength of the apparatus used. It was necessary that the apparatus should be very strong.

Mr. Rayner remarked that he had worked at the subject, and obtained results with alternating currents in agreement with those got by Watson with direct currents.

Dr. R. S. Willows pointed out that the path of the spark at the minimum sparking potential was not necessarily the shortest path between the electrodes. With regard to abrasion of the electrodes due to the electrostatic field, he referred to recent experiments which had been carried out on the subject.

The Author, in reply to Dr. Chree, stated that in the experiments with electrodes at microscopic distances apart, the restoring force which balanced the electrostatic attraction was due to a want of rigidity both of the framework of the apparatus and of the electrodes. In certain cases he would expect that the length of the free ends would have an appreciable effect on the result. In his opinion it was simply a case of electrostatic attraction, the abrasion of the surfaces not occurring until there was contact. Taking into account this attraction, the existence of a minimum spark potential, and the dielectric coefficient of the medium in which the electrodes were immersed, the experimental results could be satisfactorily explained. In reply to Mr. Rayner, he stated that the formulæ gave results which were in good agreement with those obtained both by Watson and Rayner. This was interesting, as the former obtained his results by noticing the voltage at which the capacity current suddenly increased, and the latter by studying the wattmeter readings. Recent research has shown that the voltages between overhead wires at which luminous effects, disruptive discharges, sudden increases in the readings of the ammeters and wattmeters in circuit, and sudden violent ionisation begin, are practically the same.

A paper on "*The Afterglow of Electric Discharge*" was read by Prof. R. J. Strutt.

It has long been known that when the electric discharge has passed at low pressure through certain gaseous mixtures, a luminosity survives for some seconds after the discharge has been turned off. A greatly improved method of experimenting on the phenomenon was introduced by Dewar (*Proc. Roy. Inst.*, 1888). A powerful air-pump is used to draw a regulated current of gas through the vacuum tube. In this way a continuous removal of the gas from the region of discharge is effected, and the afterglow which it emits in passing through another vessel on its way to the pump can be examined continuously and at leisure.

There has been considerable difference of opinion as to whether pure oxygen shows a glow or not. Under the conditions of the author's experiments the glow, if any, is certainly exceeding faint. With air, on the other hand, a bright yellow glow is obtained, which is improved by enriching the air with oxygen. Pure nitrogen gives no glow whatever.

Several previous experimenters have connected the glow with ozone, though generally without expressing any very definite view as to what part ozone played in its production. The chief evidence for this hitherto has been that the glow is only obtained where oxygen is present, and that it is destroyed by heat. The following additional evidence was obtained:—

1. The glow cannot survive passage through a tube cooled in liquid air. This is regarded as due to condensation of ozone.

2. It is destroyed by passage over oxides of copper, manganese, and silver. Ozone, too, is known to be destroyed by these substances.

3. While the glowing gas oxidises bright silver, the gas current beyond the point at which the glow has died out does not do so. Disappearance of the glow is simultaneous with disappearance of ozone from the gas.

The glow is thus shown to involve consumption of ozone. It is therefore natural to regard it as a flame of low temperature, arising from the oxidation of some other body by ozone. The next experiments were made to determine the nature of this other body. A current of ozone from a vacuum tube fed with oxygen was allowed to mix, in a Y-shaped tube, with any other gas which it was desired to test, on its way to the pump.

Nitrogen or ordinary air added to the ozone gave no effect, but air, which had been through an independent discharge, and had been deprived of its original glow by silver oxide, was found to glow again on mixing with ozone. Clearly then some body is produced in air by the discharge whose oxidation is responsible for the glow.

This body proves to be nitric oxide. On leading a current of this gas into the ozone stream a very brilliant glow was obtained, of the characteristic yellow colour. By suitable arrangements this glow can be produced in the form of a pointed flame, with dark inner cone. The glow is not associated with a sensible rise of temperature Condensing the ozone with liquid air, allowing it to re

evaporate, and admitting nitric oxide to it, a yellow flash can be obtained, long after the electric discharge is over. The glow is purely chemical in its origin.

Ozone from the Siemens tube used at atmospheric pressure seems incapable of yielding the glow when mixed with nitric oxide. This may be due to the low percentage of ozone present. Further investigation is in progress on this point, and also on the possible production of a glow in other cases of oxidation by ozone.

The main conclusion of the present paper is that the ordinary yellow afterglow is due to oxidation of nitric oxide by ozone.

Dr. J. A. Harker asked if the presence or absence of water-vapour had any effect upon the results obtained.

The Author replied that the same results were obtained with air saturated with water-vapour and air dried by means of phosphoric anhydride.

Mr. J. S. Dow described a form of instrument, of specially portable and compact design, for the measurement of surface brightness or illumination. The observer looks through an aperture in a white screen, which is illuminated by means of a small glow-lamp, at the surface to be studied. The illumination of the screen can then be varied by a special device which gives a uniform scale capable of being calibrated in foot-candles or lux, as desired. The instrument can be calibrated by observing any surface of known brightness and a range of readings from 0·01 to 100 foot-candles can be secured. For this purpose two neutral dark glasses, each reducing the incident light to 1/10th, are employed.

The device for adjusting the illumination of the screen in the apparatus is as follows:—The small glow-lamp is set within a light-tight white chamber and illuminates a ground opal sector-shaped piece of glass at the end of it, with uniform intensity. Shutters can then be caused to travel in front of this glass, cutting off the area to a known extent and causing a corresponding change in the resultant illumination. The author referred to several sources of error encountered and overcome in order to secure the requisite uniformity and an accurate scale of foot-candles.

Subsequently the author mentioned some experiences in using the instrument, which can be readily carried about by the observer into any interior and applied to measure illumination or surface brightness in any plane, and in inaccessible places. The instrument, it is suggested, will also be of service in the laboratory on account of its simplicity and ease of manipulation.

Dr. Russell thought that a photometer of this nature would prove of great value to medical inspectors of schools. It would furnish a means also of telling whether the photometrical observations of street lighting on foggy nights were much affected by absorption.

A paper on "*The Approximate Solution of various Boundary Problems by Surface Integration combined with Freehand Graphs*," by Mr. L. F. Richardson, was taken as read.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, December 5th, 1910.

Mr. E. Grant Hooper in the Chair.

The following papers were read and discussed:—

"*Analytical Constants of Shellac, Lac Resin, and Lac Wax.*" By Puran Singh.

The author has examined samples of the following kinds of pure shellac:—"Kusumi lac" (from *Schleichera triguga*), "Palas lac" (from *Butea fondosa*), and "block" (or coagulated lac), which had been prepared by himself by extraction of the crude lac with wood spirit. A sample of pure lac prepared in a well known factory was also examined.

He confirms the view that Parry's figures and his method of estimating resin, which is the most frequent impurity, by means of the iodine absorption of the sample, are the mosr reliable which are available. His own samples were examined for moisture, solubility in hot alcohol, acid number, saponification number, iodine value (Hübl), and also for a new constant, namely, the percentage of non-condensable resin and fatty acids as recently proposed by Dr. H. Endemann.

The analytical figures for lac wax and lac resin are given by the author, who discusses the significance of the various results.

"*Theory of Dyeing: Resolution after Treatment or Acids, &c.*" By W. P. Dreaper, F.I.C., and A. Wilson, B.Sc.

In this paper the authors' method of examining the state of the dye on a fibre is applied to samples dyed with acid dyes in acid solutions, which lead to a greater absorption of the dye by the fibre. It is shown that the extra dye fixed through the presence of acid is not fast against resolution into alcohol or soap solution, and that therefore the important factor in dyeing from this point of view is the temperature of dyeing. Ninety per cent instead of 20 per cent of the dye may be removed when dyeing takes place at 18° instead of 100° by subsequent resolution. Different acids seem to act in proportion to their combining weights. Dyeing with acid colours in alkaline solutions is shown to be possible, and that in strong solutions less dye is required to obtain the standard shade than in weak ones. This is unexpected, and indicates the very complicated nature of dyeing reactions. Abnormal results are also shown when resolution takes place. This depends upon the nature of the solvent with the same dye, and the variations depend upon the conditions and nature of the dye solution in a remarkable manner.

When dyeing takes place in alkaline solution the dye is very fast, comparatively speaking, against resolution into alkaline solution, but not so fast as when dyed in acid when resoluted into alcohol. The fastness gains in one direction and decreases in another, according to the nature of the dye-bath. The experiments are being extended to cover other classes of dyes.

"*Some Indian Oils and Fats.*" By Ambat Kesava Menon, B.A.

Of the following Indian fats and oils, the last eight have been investigated for the first time:—Cow ghi, buffalo ghi (ghi = clarified butter-fat); fats from the seeds of *Bassia butyracea*, *Bassia latifolia*, *Bassia longifolia*, *Payena oleifera*; oils from the seeds of *Jatropha glandulifera*, *Luffa acutangula*, *Mimusops elengi*, *Pithecolobium dulce*, *Psoralea corylifolia*, *Sapindus trifoliatus*, *Thespesia populnea*, and *Vernonia anthelmintica*. The oils of the Bassia family (sold in India under such names as Elupai, Illupai, Mowa, Mowrah, &c.) are gaining commercial importance; already considerable quantities of the seeds are exported to European countries, where fats obtained therefrom find application in soap and candle industries. The export trade in these seeds in 1908-9 reached £166,161.

The seeds and oils, which have been examined for the first time, were received from the Government Museum, Madras. Hitherto no efforts have been made in India to prepare the oils for other purposes than for medicinal use. As large quantities of these seeds are available, there would seem to be a prospect of exploiting them commercially.

RÖNTGEN SOCIETY.

At the meeting of the Röntgen Society on December 1st, Dr. W. Deane Butcher delivered a lecture on "Osmotic Growths," a subject which he has been studying in collaboration with Professor Stéphane Leduc, of Nantes. Osmotic, he pointed out, meant "pushing, or thrusting," and the curious growths he had to show were in reality mineral growths due to osmotic pressure. He recalled the work on spontaneous generation with which the name

of Mr. Butler Burke was associated so prominently five years ago, and said that Burke's term "radiobe" might be adopted to describe the phenomena obtained by Leduc and himself. The growths which resulted from osmotic pressure were mineral radiobes. They were mineral productions growing without the stimulus of germs or even of radio-activity. A typical means of production, which he showed by way of experiment at the meeting, was to place a lump of calcium chloride freshly fused from the furnace, and free from any trace of life or germ or organic matter, and drop it into a solution of silicate of soda which had also been sterilised by heating. Within a few moments the calcium chloride would be observed to grow, and it would grow in such a manner as to suggest irresistibly an organic growth, although, of course, greatly quickened in its process. It would put forth a stem having a structure very like that of a tree, and this would grow up, not gradually but in a series of jerks and pushes, until on reaching a layer of the solution which was somewhat less dense than that through which it had passed, it would send out branches again very like those of a tree. By varying the minerals and solutions employed, an extraordinary variety of growths could be obtained, many of them simulating natural organisms. Nitrate in solution always gave a curious spiny projection. In Dr. Butcher's view, when the chloride of calcium was dropped into the sodium silicate solution, the water tore apart some of the molecules of the former, and the ions being set free to roam through the gas—he called it gas because osmotic pressure showed the same volume and temperature relationships as gaseous pressure, had the same absolute value, and was indeed gaseous pressure in disguise—they formed a precipitate with the ions of the silicate. According to Leduc, the field of liquid diffusion was very like an electric field in that it had positive and negative centres of diffusion and concentration. By taking advantage of these phenomena, and dropping certain chemical substances into the solution—nothing, however, that was not found in the organic structure it was hoped to simulate—these when broken up by the two poles of diffusion would give markings and colours corresponding in a remarkable manner to those of a butterfly's wing or a peacock's tail or the plumage of a humming-bird. Hematin, again, in certain solutions would produce shapes not unlike the corpuscles of the blood.

As to the bearing which the phenomena seen under osmotic pressure had upon the question of the mechanism of life, Dr. Butcher said that he did not suggest that osmotic growths were living organisms. Nor did he think that the question of life need enter into the matter at all. But in the osmotic growth they had a picture of the machinery which Nature employed in her growing or productive processes. Osmotic pressures were substantially the same force as that which lifted the sap in the tree or forced the plant through the soil. In his theory the dust from which the living being drew its energy, and to which it returned it, was more vitally concerned in the activity we called life than we had yet realised. We talked of germs, but the function of the germ was only to play Prince to the Sleeping Beauty, and to waken and re-awaken the life that lay dormant in the mineral dust. Huxley's piece of chalk which had once, through the myriad of micro-organisms that now lay frozen within it, enjoyed a carnival of life might live again. And what they saw when that piece of chalk was turned into calcium chloride, and on being placed in a sodium silicate solution grew before their eyes, was, in his judgment, a rapid and rough illustration of the method employed by Nature in the continual renewal of the vitality that lay, supposedly dead and inert, in the dust of the earth.

Hydration of Metaphosphoric Acid.—D. Balareff.—When metaphosphoric acid is hydrated in aqueous solution at different temperatures and concentrations it passes directly into the ortho-acid, no trace of pyro-acid being detected by analytical methods.—*Zeit. Anorg. Chem.*, No. 3.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cli., No. 17, October 24, 1910.

Constituents of Coco Essence.—A. Haller and A. Lassieur.—The investigation of essence of coco shows that, apart from the acids separated by alkalis, which may result from the saponification of fatty substances, the following compounds are present: — (i.) Methylheptyl, methylnonyl, and methylundecyl ketones, the second of these constituting about 75 per cent of the mixture. (ii.) Dextro-methylheptyl and methylnonyl carbinols, *i.e*, the optical inverses of the alcohols found in essence of rue. (iii.) An unknown aldehyde.

Nitrous Ethers of Cellulose.—Paul Nicolardot and Georges Chertier.—To prepare nitrous ethers of cellulose it is best to allow nitrous vapours to act upon it in a nitric medium. With dilute acid a large quantity of nitrous ethers mixed with nitric ethers containing only a little nitrogen is obtained. With stronger nitric acid a smaller yield of nitrous and nitric ethers is obtained. These nitrous ethers can be separated from the nitrites by dissolving in acetone in which only the former are soluble. The nitrous ethers are easily saponified by water at the ordinary temperature. Concentrated acids, except acetic acid, saponify them in the cold.

Zeitschrift für Anorganische Chemie. Vol. lxviii., No. 3, 1910.

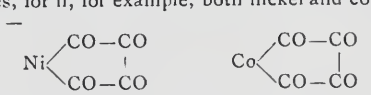
Purification of Colloids by Dialysis.—R. Zsigmondy and R. Heyer.—In experiments in which the suitability of different membranes (parchment, collodion, fish-bladder, &c.) for dialysis was tested it was found that fish-bladder is superior to the other membranes. The progress of the purification of colloidal silicic acid was tested from time to time, and it was found that by dialysis with frequent change of water chlor-ions can be practically removed in a few days. The experiments were repeated in dialysers in which the water was continually changed, and the same results were obtained. A new dialyser was constructed in which the large water holder of the ordinary form was replaced by a cylindrical vessel of large sectional area and small altitude, and the layer of water was rapidly replaced by a current of fresh water. This new form of apparatus enables colloids to be purified by dialysis much more rapidly than in the old form.

Binary Systems of Calcium Metasilicate with Calcium Fluoride and Calcium Chloride.—B. Karandéeff.—Calcium metasilicate and fluoride do not form a compound with one another. The eutectic corresponds to about 48 mol. per cent of calcium fluoride or 38·2 parts by weight per cent of calcium fluoride; the eutectic temperature is 1130°, and the eutectic consists of calcium fluoride and wollastonite. Calcium metasilicate and calcium chloride do not form any compound. The eutectic contains only very little $CaSiO_3$, and the eutectic temperature lies about 8° below the melting-point of calcium chloride (772°). Between 30 and 40 mol. per cent CaF_2 (about 1200°) and between 50 and 60 mol. per cent $CaCl_2$ (about 1150°) there is a sharp change in the structure of the conglomerate, which is probably due to the transformation of pseudowollastonite into wollastonite.

Silver-cadmium Alloys.—G. Bruni and E. Quercigh.—From the melting-point curves of silver-cadmium alloys the authors have found that mixed crystals exist containing from 0—80 and from 87—100 atoms per cent Cd. Two compounds exist, viz., AgCd and $AgCd_4$. Alloys of

80—87 atoms per cent Cd in the solid state form an agglomerate of $AgCd_4$ and mixed crystals.

New Metal Carbonyls.—Ludwig Mond, Heinrich Hirtz, and Matthewman Dalton Cowap.—When carbon monoxide acts on nickel, cobalt, iron, and molybdenum at high pressures the following metallic carbonyls are formed: —$Ni(CO)_4$, $Co(CO)_4$, $C_2(CO)_3$, $Fe(CO)_5$, $Fe_2(CO)_9$. $Fe(CO)_4$, $Mo(CO)_6$. Ruthenium also forms a compound. These carbonyls bear a strong resemblance to one another chemically. They decompose into carbon monoxide and the metal on heating, the metal being precipitated in the form of a bright metallic mirror. Acids which do not oxidise do not attack them, but oxidising acids rapidly dissolve them; the aqueous solutions of the halogens act on them very quickly with evolution of carbon monoxide. At least one carbonyl of each metal can be volatilised without undergoing decomposition, and can be purified by distillation or sublimation. They are all more or less soluble in the ordinary organic solvents, such as ether, alcohol, benzene, &c., and insoluble in water. As regards physical properties the carbonyls are very different; thus nickel tetracarbonyl (a liquid which evaporates very quickly) has a specific gravity 1·32, while diferroenneacarbonyl has a specific gravity 2·085. Some carbonyls can be obtained in the gaseous, liquid, or solid state, others only in the solid and gaseous states, and others only as solids. It is exceedingly difficult to find a general chemical formula for these compounds. It cannot be assumed that all the carbonyls are directly bound to the iron, as then the valencies of cobalt would be 8 and 6, and those of iron 8, 9, and 10. A cyclic formula does not explain all their properties, for if, for example, both nickel and cobalt tetracarbonyl—



are supposed to have the same constitution, it is difficult to understand why the cobalt compound should have the double molecular weight in benzene solution, and why one of its carbonyl groups can be split off more easily than the others. Moreover, the compound $Fe_2(CO)_9$ cannot belong to the same series as the others. It appears probable that the compounds have a molecular rather than an atomic composition, the carbonyl taking the place of water of crystallisation, or of hydration, but this assumption is contradicted by the fact that the gaseous compounds have the normal gas densities.

Heat Evolved by the Decomposition of Ozone.—Anton Kailan and Stephan Jahn.—The heat evolved when ozone is decomposed at constant volume is 34.500 calories per grm.-molecule, this result being accurate to ± 1 per cent. The experiments were performed using soda lime as a catalyser. With other catalysers, *e.g.*, platinum black, rather higher values were obtained.

Researches on the Complexity of Tellurium.—W. R. Flint.—A large quantity of tellurium of atomic weight 127·5 was prepared. After ten hydrolytic fractionations with hot water of a solution of this preparation in hydrochloric acid, a product was obtained which consisted of the dioxide. The atomic weight of the tellurium of the tenth fraction was 124·3. Atomic weight determinations with the intermediate fractions gave 126·6 and 125·4, and thus a progressive lowering of the atomic weight occurs. Thus 124·3 appears to be the nearest approximation yet reached to the atomic weight of elementary tellurium. Fractionation by the hydrolysis of the nitrate was next attempted, but it is impossible to say from the results at present obtained whether this method is more rapid than the hydrolysis of the chlorine. The reactions of the less easily hydrolysed part agree with those of tellurium except in one particular.

Gravimetric Determination of Vanadium as Silver Vanadate.—Philip E. Browning and Howard E. Palmer.—Vanadium can be determined as silver vanadate if to a neutral solution of ammonium vanadate nitric acid is added, and then ammonium hydroxide, and the solution is then boiled to expel the ammonia. Silver nitrate is then added in excess to the boiling solution.

MISCELLANEOUS.

The Physical Society's Annual Exhibition.—This Exhibition, which is to be held on Tuesday, the 20th inst., will be opened in both the afternoon (from 3 to 6 p.m.) and in the evening (from 7 to 10 p.m.). Prof. J. A. Fleming, F.R.S., will give a discourse at 4·15, and again at 8 p.m., on "Some Improvements in Transmitters and Receivers for Wireless Telegraphy"; and Mr. R. W. Paul will give a number of cinematograph demonstrations of some "Physical Phenomena." The following firms will be exhibiting:—R. and J. Beck, Ltd.; British Radio-Telegraph and Telephone Co., Ltd.; Cambridge Scientific Instrument Co.; Casella and Co.; A. C. Cossor, Ltd.; H. W. Cox and Co., Ltd.; Crompton and Co., Ltd.; J. H. Dallmeyer, Ltd.; Elliott Bros.; Everett, Edgcumbe, and Co.; Gallenkamp and Co.; Gambrell Bros.; J. J. Griffin and Sons; Hicks and Co.; A. Hilger, Ltd.; Indiarubber, Guttapercha, and Telegraph Works, Ltd.; Marconi's Wireless Telegraph Co.; Leslie Miller; Muirhead and Co.; Nalder Bros. and Thompson; Negretti and Zambra; Newton and Co.; R. W. Paul; W. G. Pye and Co.; Strange and Graham; H. Tinsley; Townson and Mercer; Weston Electrical Instrument Co.; Wright and Co.; Carl Zeiss. We understand that invitations have been given to the Institution of Electrical Engineers, the Faraday Society, the Optical Society, and the Röntgen Society. Admission in all cases will be by ticket only, and therefore members of the Societies just mentioned (including also the Physical Society) desiring to attend the Exhibition should apply to the Secretary of the Society to which they belong.

The Franklin Institute. Award of Medals.—Recommendations to the Science and Arts Committee of the Franklin Institute of its Special Committee on the Award of the Elliott Cresson Medal to Distinguish Scientists and Technologists:—

For "distinguished leading and directive work in electrical discovery and in the advancement of electrical application," to Edward Weston, Esq., D.Sc., LL.D., Newark, N.J.

For "distinguished leading and directive work in the advancement of our knowledge of the physical sciences," to Joseph John Thomson, D.Sc., LL.D., Knight, Cavendish Professor of Experimental Physics, Cambridge University, England.

For "distinguished leading and directive work in the advancement of our knowledge of metallurgical science," to Robert A. Hadfield, D.Sc., LL.D., Knight.

For "distinguished leading and directive work in the fields of agricultural and physiological chemistry," to Harvey W. Wiley, Esq., M.D., Ph.D., LL.D., Chief Chemist to the Department of Agriculture, Washington, D.C.

For "distinguished leading and directive work in the development of the iron and steel industries," to John Fritz, Esq., Bethlehem, Pa.

For "distinguished leading and directive work in the production and perfection of instruments for astronomical research," to John A. Brashear, Sc.D.,, LL.D., of Pittsburgh, Pa.

MEETINGS FOR THE WEEK.

Tuesday, 20th.—Physical, 3 and 7. Exhibition of Electrical, Optical, and other Physical Apparatus at the Imperial College of Science. Experimental Discourse on Detonators, by Dr. J. A. Fleming.

Wednesday, 23rd.—Microscopical, 8. "Modern Methods of Research on a Scientific Cruiser" (illustrated by Lantern Slides), by A. Earland.

THE CHEMICAL NEWS.

Vol. CII., No. 2665.

NITROFORM AND TETRANITROMETHANE.

By F. D. CHATTAWAY, F.R.S.

Nitroform and tetranitromethane were first obtained about the middle of last century by Schischkoff, who was then engaged in the study of mercuric fulminate. This compound served as the starting-point in both preparations; it was first converted by heating with an aqueous solution of sodium chloride into sodium fulminurate, and from this trinitroacetonitrile nitroform and tetranitromethane were successively produced.

Schischkoff (*Ann. Chim. Phys.*, 1857, [3], xlix., 310) prepared trinitroacetonitrile by adding sodium fulminurate little by little to a mixture of equal volumes of fuming nitric and sulphuric acids. As the liquid became warm carbon dioxide was disengaged, while ammonium salt and trinitroacetonitrile, which collected as an oily layer on the surface, were formed. The action may be representsd thus:—

$$H_3C_3N_3O_3 + 2HNO_3 = C(NO_2)_3CN + CO_2 + NH_3 + H_2O.$$

When about 12 grms. of fulminurate had been added the vessel containing the mixture was cooled until the oily layer solidified and could be removed. It was finally distilled in a current of dry air at a temperature of about 60°, when it solidified in the neck of the retort as a mass of white crystals, the yield being about two-thirds of the weight of sodium fulminurate used.

Trinitroacetonitrile thus obtained is a very volatile white solid, somewhat resembling camphor in appearance; it melts at 41·5 and explodes when quickly heated to about 220°.

Trinitroacetonitrile is rapidly hydrolysed by hot water, carbon dioxide being formed together with the ammonium salt of trinitromethane,—

$$C(NO_2)_3CN + 2H_2O = CO_2 + C(NO_2)_3NH_4.$$

The latter salt may be obtained in well-formed yellow crystals by evaporating down the solution. With aqueous potash, potassium carbonate and the potassium salt of trinitromethane are similarly obtained.

Schischkoff found that when either of these salts was added to sulphuric acid, nitroform separated as a liquid layer, which solidified on cooling to a mass of white crystals fusible by the heat of the hand.

Thus prepared, nitroform is a colourless substance solid below 15°, and crystallising well in cubes or perhaps very obtuse rhombohedra. It cannot be distilled under ordinary pressure, for at 100° a vigorous reaction takes place in which much gas is liberated, which carries away a great part of the nitroform not decomposed.

Schischkoff (*Ann.*, 1861, cxix., 247) soon discovered that the hydrogen atom of nitroform could be replaced by a fourth nitroxyl group. This replacement he effected by adding nitroform to a similar mixture of nitric and sulphuric acids, and leading through the mixture, heated to 100°, a stream of air. A liquid distilled over which, on dilution with water, deposited tetranitromethane as an insoluble heavy liquid. When separated, washed with water, and distilled, tetranitromethane was obtained as a colourless mobile liquid, boiling at 126° and solidifying at 13° to a crystalline mass.

Tetranitromethane is notably more stable than nitroform; even when the vapour is strongly heated it does not explode, but decomposes with evolution of nitrous fumes.

The nitration of nitroform remained the only known method of making tetranitromethane until 1903, when Pictet and Genequand (*Ber.*, 1903, xxxvi., 2225) found that it was formed in small amount by the interaction of acetic anhydride and diacetylorthonitric acid. The latter substance they obtained as a liquid boiling constantly at 127·7 at 730 mm. pressure, by mixing ordinary nitric acid of sp. gr. 1·41 with an equal volume of acetic anhydride, and fractionally distilling. They assigned to it the formula $(CH_3.COO)_2N(OH)_3$, regarding it as a mixed anhydride of acetic acid and ortho nitric acid, $N(OH)_5$, the existence of which in dilute nitric acid they assume.

Desiring to withdraw a molecule of water from this diacetylorthonitric acid, they allowed it to act upon an equivalent quantity of acetic anhydride. The reaction proved especially violent, the heat developed causing vigorous ebullition, while torrents of red fumes were evolved. On distilling the product, acetic acid came over containing in solution a little tetranitromethane, which was deposited as oily drops on adding water. The yield was very small, as might be expected from the oxidation which must have occurred considering the violent evolution of oxides of nitrogen.

Pictet and Genequand found that traces of tetranitromethane were produced when fuming nitric acid was added to acetic anhydride, but they state that the action is dangerously violent, explosions accompanied by flame often occurring.

Classen in 1907 patented a process (D.R.P. 184229; *Journ. Chem. Soc.*, 1907, *Abstracts*, i., 885) founded on the observation that tetranitromethane is formed when aromatic hydrocarbons or their derivatives are heated with a very large excess of a mixture of nitric and sulphuric acids containing a considerable amount of sulphur trioxide. He recommends distilling 70 grms. of nitrobenzene with something over 2 kilogrms. of the mixture for eight to twelve hours.

Two further patents were taken out in 1909 by Schenck (D.R.P. 211198 and 211199; *Journ. Chem. Soc.*, 1909, *Abstracts*, i., 689), who protected a process in which a satisfactory yield of tetranitromethane was obtained by slowly dropping acetic anhydride into a mixture of nitrogen pentoxide and nitrogen peroxide.

It is obvious that all these processes leave much to be desired in the way of simplicity, and during the present year directions for preparing the compound in a simple manner from nitric acid and acetic anhydride have been published by Chattaway (*Proc. Chem. Soc.*, 1910, xxvi., 164), and by Baeyer and Co., of Elberfeld (D.R.P. 224057).

The operations necessary in the method are so simple and so easily carried out that the preparation is well adapted to take its place in any elementary course of practical organic chemistry to illustrate the ease with which aliphatic compounds can be nitrated, whilst the materials employed are so cheap and the yield is so satisfactory as to make tetranitromethane, which has hitherto been a somewhat unfamiliar substance, one of the most easily procurable of organic compounds.

Chattaway (*Journ. Chem. Soc.*, 1910, xcviii., 2099) recommends the following procedure for preparing tetranitromethane on a small scale:—Place 31 grms. of nitric acid, sp. gr. 1·53, in a 250 cc. flask, and add gradually 50 grms. of acetic anhydride in quantities of about 2 cc. Some little heat is developed, especially at first, and the flask should therefore be cooled in a basin of water, otherwise the action may become too vigorous. It is not advisable to let the temperature rise much above 20—25° C.

When all the anhydride has been added, cover the flask loosely by a watch-glass or inverted small beaker, and allow it to remain at the ordinary temperature of the laboratory for a week. As action proceeds carbon dioxide is continuously but very slowly evolved, and the mixture, which at first is colourless, becomes brown owing to the formation in small quantity of oxides of nitrogen. After the expiry of a week the tetranitromethane which remains dissolved in the acetic acid may be separated by pouring the mixture into about 150—200 cc. of water. The

bulk of the tetranitromethane separates in small drops, and subsides in a colourless heavy oily layer which can be withdrawn by a tap funnel. A further small quantity still remaining dissolved in the dilute acetic acid may be recovered by blowing steam for a few minutes through the liquid; the tetranitromethane, which distils easily in steam, comes over with the first few cc. of the distillate. The tetranitromethane thus prepared may be freed from traces of acid by washing with water and very dilute sodium carbonate solution, or even better, though with some slight loss, by distilling in steam. It is then only necessary to dry it over fused calcium chloride. A yield of 18 to 20 grms. should be obtained.

Tetranitromethane is a heavy mobile liquid of a very faint yellow colour, which boils at 126° under ordinary pressure, though with slight decomposition, and solidifies at 13° to a white crystalline mass. It has a density of 1·65, and is readily soluble in alcohol and ether, but not in water.

The anhydrous nitric acid required in the preparation is most easily obtained by slowly distilling ordinary fuming nitric acid from its own bulk of strong sulphuric acid. If ordinary concentrated nitric acid (sp. gr. 1·41) is used it is best to distil it twice from sulphuric acid. It is not necessary, though advisable if convenient, to distil off the acid under diminished pressure.

There is no great advantage in freeing the anhydrous nitric acid thus prepared from oxides of nitrogen, as even if the acid is colourless when added to the acetic anhydride, and the mixture is kept at 0° in a dry atmosphere, it becomes coloured by the formation of such oxides in small amount in a few days.

The yield is somewhat better if no oxides of nitrogen are present, but this slightly increased yield does not compensate for the extra labour involved in the preparation of the acid.

The action takes place almost quantitatively according to the equation—

$$4(CH_3CO)_2O + 4HNO_3 = C(NO_2)_4 + CO_2 + 7CH_3COOH;$$

a small amount of the tetranitromethane is, however, carried away as the very heavy vapour by the escaping carbon dioxide, and a further small quantity is lost during the separation.

When nitric acid attacks acetic anhydride a mono-nitro derivative is probably first produced, which is nitrated so much more readily than the parent compound that action proceeds until the three hydrogen atoms of a methyl group have been replaced. The tri-nitro acetic acid formed by hydrolysis then slowly decomposes into carbon dioxide and nitroform, which, as soon as it is liberated, is converted by the remainder of the nitric acid into tetranitromethane.

This explanation of the course of the reaction is supported by the circumstance that when a freshly made mixture of nitric acid and acetic anhydride is heated, a very violent action occurs, during which torrents of nitrous fumes are evolved while very little tetranitromethane is formed. This violent action must be due to the nitroform immediately it is liberated breaking down rapidly, as it does when heated alone to about 100°, very little in consequence being further nitrated.

The ease with which tetranitromethane can thus be obtained renders it possible to prepare nitroform and its salts with little trouble by a method which we owe to Hantzsch and Rinckenberger (*Ber.*, 1899, xxxii., 628). These chemists found that the potassium salt of nitroform is produced quantitatively, together with ethyl nitrate when tetranitromethane is allowed to act upon alcoholic potash,—

$$C(NO_2)_4 + C_2H_5OK = C(NO_2)_3K + C_2H_5.ONO_2.$$

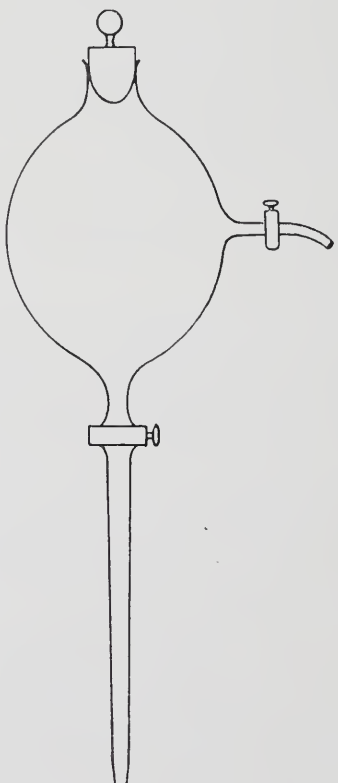
They recommend adding the theoretical quantity of tetranitromethane to a cooled alcoholic solution of potassium hydroxide, or better potassium ethylate, when potassium nitroform separates out at once as a yellow crystalline precipitate, which, after washing with alcohol and ether, is quite pure.

On adding this salt in small portions to strong sulphuric acid, nitroform is liberated and rises to the surface, where it collects as a mobile colourless liquid which may be separated by a tap funnel. If necessary ether may be added, the ethereal solution being then dried over fused calcium chloride and the solvent allowed to evaporate in a vacuum. Nitroform thus obtained is at the ordinary temperature a somewhat volatile oily liquid of disagreeable smell. If traces of moisture are present, it is somewhat yellowish in colour, but after having been solidified in a freezing mixture and pressed upon porous porcelain, it is obtained as a colourless solid melting at 15°. It has a strong acid reaction and taste, and is miscible with water.

A MODIFIED SEPARATORY FUNNEL AND WASHER FOR HEAVY LIQUIDS.

By H. M. ATKINSON.

An ordinary tap funnel with a second tap and short tube inserted about half-way up the side, as shown in figure, serves well for washing heavy liquids, as aniline, &c. The wash-water, solution of soda, &c., can be run off by the side-tap, and fresh water added, and shaken, &c., without the necessity of running off the heavy liquid into a



second flask or funnel. In fact, the drying with calcium chloride can also be performed in the funnel itself. Messrs. Baird and Tatlock made me a funnel as described above; a simpler form with a short tube, to be closed by a piece of rubber and pinchcock, would also serve in many cases.

Limerick Technical Schools

REPORT ON GASEOUS COMBUSTION.*

By WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S.

(Continued from p. 298).

Section V.—*The Combustion of Hydrocarbons.*

The question of how a hydrocarbon is attacked by oxygen in combustion has been the subject of much controversy during the past twenty years, but it is only quite recently that experimental inquiry has been pushed far enough to justify the advancement of any complete theory of the process.

Throughout the greater part of last century it was accepted as an article of faith among chemists that hydrogen is the more combustible element of hydrocarbon; thus, as late as 1884 H. B. Dixon, in his Cantor lectures on "The Use of Coal Gas," speaking of the combustion of ethylene in its bearing on the luminosity of hydrocarbon flames, said:—"This ethylene, when it is raised to a high temperature in contact with air, is decomposed, the hydrogen burning first and the carbon afterwards. There is a race for the oxygen of the air between the two constituents of the ethylene, and the hydrogen, being the fleeter of the two, gets to the oxygen first, and is burnt to water." Eight years later, when it was discovered in Dixon's laboratory that an equimolecular mixture of ethylene and oxygen yields on detonation almost exactly twice its own volume of carbon monoxide and hydrogen (H. B. Dixon, *Phil. Trans.*, 1893, 159; also Lean and Bone, *Trans. Chem. Soc.*, 1892, lxi., 873), in accordance with the empirical equation $C_2H_4 + O_2 = 2CO + 2H_2$, and also that an equimolecular mixture of acetylene and oxygen behaves similarly (Bone and Cain, *Trans. Chem. Soc.*, 1897, lxxi., 26), $C_2H_2 + O_2 = 2CO + H_2$, the dogma of the preferential combustion of hydrogen became untenable. Attempts were then made to revive an idea originally put forward by Kersten in 1861, namely, that "before any part of the hydrogen is burnt all the carbon is burnt to carbonic oxide, and that the excess of oxygen (if any) divides itself between the carbonic oxide and hydrogen." H. B. Dixon was himself inclined to this view, and Smithells definitely pronounced for it in his lecture on "Flame" at the Nottingham Meeting of the Association in 1893.

The idea of a "selective" combustion, whether of carbon or of hydrogen, is, however, so repugnant to well-established principles that it could hardly be expected to meet with general acceptance in any final or complete sense, and there were many sceptics as to its validity. Moreover, whilst in the cases of acetylene and ethylene the assumption of a *direct* transition from the system $C_nH_m + n/2O_2$ to $nCO + m/2H_2$ implies a simple transaction from the kinetic standpoint, an extension of the idea to the cases of such hydrocarbons as propane or propylene would obviously raise serious difficulties—

$$2C_8H_8 + 3O_2 \quad 6CO + 8H_2,$$
$$2C_3H_6 + 3O_2 \quad 6CO + 6H_2.$$

It therefore seemed necessary to consider whether the solution of the problem might not lie in the assumption of an initial association of the hydrocarbon and oxygen forming an unstable "oxygenated" or "hydroxylated" molecule, as suggested by H. E. Armstrong many years ago, and it was with some such possibility in view that the writer undertook the re-investigation of the subject about ten years ago.

Previous workers had confined their attention to combustion at such high temperatures as prevail in hydrocarbon flames and the explosion wave—conditions highly unfavourable to the detection or isolation of unstable intermediate "oxygenated" products, if such are really formed. It was therefore decided first of all to make a systematic study of hydrocarbon combustion at temperatures below the ignition points of the mixtures used, where the rate of oxidation would be much slower and more controllable, and intermediate products more stable. The hydrocarbons selected for investigation were methane, ethane, ethylene, and acetylene, and at the outset of the work it was fortunately discovered that all four gases combined with oxygen at temperatures much below those at which either hydrogen or carbon monoxide begin to be oxidised with any appreciable velocity, or at which either carbon reduces steam or the reversible reaction $CO + OH_2 = CO_2 + H_2$ could have any influence whatever upon the result. Conditions were thus established which precluded the interference of secondary processes with the main line of change.

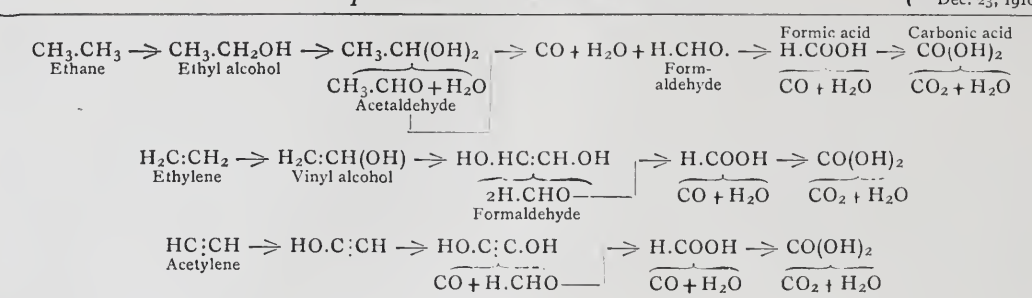
The first experimental method consisted in maintaining mixtures of each hydrocarbon with varying proportions of oxygen, sealed up in borosilicate glass bulbs of about 60 cc. capacity, at known constant temperatures between 250° and 350°, for definite periods of time. Subsequently an apparatus was devised in which large volumes of the reacting mixtures could be circulated at a uniform speed in a closed system comprising (1) a surface of porous porcelain maintained at a constant temperature in a combustion furnace, (2) suitable cooling and washing arrangements for the removal of condensable or soluble intermediate products, and (3) a mercurial manometer for recording pressures.

By means of these two experimental methods it was proved, as regards slow combustion—(1) That a hydrocarbon is ultimately burnt to a mixture of steam and oxides of carbon without any separation of carbon or liberation of hydrogen at any stage of the process; (2) that the oxidation is marked by a very large intermediate formation of aldehydic products; (3) that the fastest rates of oxidation are (in the cases of the four hydrocarbons examined) always obtained with a ratio of hydrocarbon to oxygen between 2 : 1 and 1 : 1, an excess of oxygen above the equimolecular ratio always having a marked retarding influence; and (4) that a large proportion of carbon dioxide is often found in the products under conditions which preclude all possibility of its formation either by the direct oxidation of the monoxide or by the interaction of the monoxide with steam.

Finally, the balance of evidence was so overwhelming in favour of the supposition that combustion had proceeded by successive stages of "hydroxylation" that the accompanying schemes were put forward for the typical hydrocarbons ethane, ethylene, and acetylene. In other words, the attack of the oxygen upon the hydrocarbon may be supposed to involve a series of successive "hydroxylations," the hydroxylated molecules either breaking down or undergoing further oxidation, according to their relative stabilities and affinities for oxygen at the particular temperature, substantially as represented by these schemes. (See next page).

It should be mentioned, however, that whilst in many of the "circulation" experiments a very large proportion of the intermediate aldehydic products were successfully removed from the sphere of action before undergoing further oxidation—*e.g.*, as much as 92 per cent of the formaldehyde indicated at the third stage of the ethane scheme, and 45 per cent of that required at the second stage of the ethylene scheme—in none of the experiments was it found possible to detect or isolate any of the *monohydroxy* derivatives which are, *ex hypothesi*, initially formed. This was perhaps hardly to be expected in the cases of ethylene or acetylene, where the monohydroxy derivative would be extremely unstable. In the case of ethylene, however, acetaldehyde, which is known to be readily formed by molecular re-arrangement from vinyl alcohol, was isolated in certain experiments. But failure to detect the formation of ethyl alcohol during the slow oxidation of ethane did at first sight seem a serious obstacle to the acceptance of the "hydroxylation" theory. This difficulty was, however, largely removed when it was subsequently found that ethyl alcohol is oxidised at a much

* Read before the British Association (Section B), Sheffield Meeting, 1910.

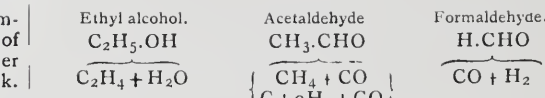


faster rate than is ethane under like conditions—a circumstance which seems to warrant the view that the effect of the initial "hydroxylation" of the hydrocarbon is to render the molecule much more susceptible to further attack. Finally, when Drugman, working in the writer's laboratory, obtained direct proof of the large formation of ethyl alcohol as the result of the interaction of ethane and ozone at 100°, the difficulty referred to entirely disappeared. Moreover, there is strong indirect proof of the initial formation of monohydroxy derivatives during slow combustion in the fact that, whereas the rates of oxidation observed with mixtures containing two molecules of hydrocarbon to one molecule of oxygen were hardly, if at all, inferior to those observed with equimolecular mixtures, the process was always much retarded by any further addition of oxygen beyond the equimolecular ratio. It may also be urged that the hydroxylation theory readily explains the large formation of carbon dioxide in the bulb experiments under conditions which would entirely preclude the idea of its formation by the direct oxidation of the monoxide or as the result of interaction of the monoxide with steam.

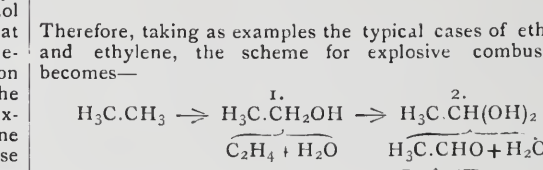
The next step in the inquiry was to ascertain whether the presence of moisture is essential to hydrocarbon combustion. A series of careful experiments on mixtures of the three typical hydrocarbons respectively with oxygen in equimolecular proportions thoroughly dried by long contact with re-distilled phosphoric anhydride, under conditions which (as was proved) inhibited the formation of steam from electrolytic gas, gave wholly negative results. If anything, combustion occurred rather more readily with the dried gases than in the case of the corresponding experiments with undried mixtures. Therefore, whilst the conclusion finally advanced concerning the mechanism of hydrocarbon combustion agrees with the view originally put forward by H. E. Armstrong, in so far as the nature of the intermediate products is concerned, it differs from his in supposing that the oxygen is *directly* active.

With the extension of the investigation to hydrocarbon flames and explosions, including "detonation" and explosions under high initial pressures, it became increasingly evident that the mechanism of combustion is essentially the same above as below the ignition-point, in so far as the result of the initial molecular encounters between hydrocarbon and oxygen is concerned. At the higher temperatures of flames secondary thermal decompositions undoubtedly come into operation at an earlier stage than in slow combustion, but they do not precede the onslaught of the oxygen upon the hydrocarbon, as was formerly supposed, but arise in consequence of it.

In considering explosive combustion, therefore, it is necessary to take into account the possible modes of decomposition of the hydroxy derivatives formed in the first two stages of slow combustion, because these derivatives are so manifestly unstable at the high temperatures of flames that they would at once break down into simpler products. *Ethyl alcohol*, it is known, decomposes into ethylene and steam; *acetaldehyde* into methane and carbon monoxide, or into carbon, hydrogen, methane, and carbon monoxide, according to the temperature; *formaldehyde* is resolved into carbon monoxide and hydrogen without the slightest separation of carbon. Thus:—



Therefore, taking as examples the typical cases of ethane and ethylene, the scheme for explosive combustion becomes—



with the proviso that, in a sufficient supply of oxygen, the transition from the hydrocarbon to the *dihydroxy* stage is so rapid that no breaking down of the molecular structure occurs in passing through the *monohydroxy* stage. When, however, the supply of oxygen is reduced below the equimolecular proportion it is evident that the initial *monohydroxy* product cannot all be further oxidised to the dihydroxy stage; some of it must therefore decompose, yielding, usually, steam as one product. It will be immediately perceived that the above theory affords a complete explanation of the well-known fact that either ethylene or acetylene on explosion with its own volume of oxygen yields carbon monoxide and hydrogen, without any separation of carbon or steam formation, because in each case the principal intermediate product is formaldehyde, a substance which decomposes straight into carbon monoxide and hydrogen at high temperatures.

There are, moreover, two groups of facts relating to explosive combustion which, whilst they completely subvert the notion of a preferential combustion of carbon, harmonise very well with the new view of "hydroxylation." They are, briefly, as follows:—(1) That whereas mixtures of olefines and oxygen corresponding to $C_nH_{2n}+n/2O_2$ behave on explosion like ethylene, inasmuch as they yield mainly carbon monoxide and hydrogen without any separation of carbon, similar mixtures of paraffins and oxygen—namely, $C_nH_{n2+2}+n/2O_2$—yield carbon, oxides of carbon, methane, hydrogen, and steam all in considerable quantities. (2) That, even in the case of an olefine, if the proportion of oxygen be reduced below that indicated by the expression $C_nH_{2n}+n/2O_2$, both carbon and steam are prominently formed.

In his presidential address to this Section at the Leicester Meeting in 1907 Smithells, whilst freely admitting the inadequacy of his former views, dissented from the writer's interpretation of explosive combustion on the ground that "the isolation of an intermediate product under one set of circumstances is in itself no proof that this product is

transitorily formed when the reaction is proceeding under another set of circumstances." To this objection it may be replied (1) that there is direct experimental proof of the formation of intermediate aldehydic products in hydrocarbon flames and explosions; (2) that notwithstanding the fact that the combustion of hydrocarbons has now been investigated over a range of temperature extending from that of incipient oxidation right up to the extreme conditions prevailing in detonation, no evidence has yet come to hand which warrants the assumption of any discontinuity in the immediate result of the initial encounter between hydrocarbon and oxygen molecules; and (3) that the theory of the intermediate formation of "hydroxylated" or "oxygenated" products furnishes a complete and sufficient explanation of the facts of hydrocarbon combustion as at present known, a requirement which no other alternative theory yet put forward is capable of satisfying. In this connection the writer is glad to find support in the recent presidential address of H. B. Dixon to the Chemical Society, where, speaking of the detonation of a mixture of equal volume of ethane and oxygen, he says:—"The ethane is not burnt wholly to carbon monoxide and hydrogen, but appears to form (as Prof. Bone has shown at lower temperatures) acetaldehyde and steam, the acetaldehyde yielding methane and carbon monoxide" (*Trans. Chem. Soc.*, 1910, xcvii., 665).

But to return to the consideration of facts:—One of the most significant features of the writer's experiments has been the proof afforded of the relatively much greater affinity of hydrocarbons, as compared with that of either hydrogen or carbon monoxide, for oxygen at the high temperatures of flames. Thus when a mixture of acetylene and electrolytic gas corresponding to $C_2H_2+2H_2+O_2$ is exploded, there is absolutely no separation of carbon or formation of steam, and practically the same thing holds good in the case of a mixture of ethylene, hydrogen, and oxygen corresponding to $C_2H_4+H_2+O_2$. In each case the hydrocarbon is burnt to (ultimately) carbon monoxide and hydrogen, just as would be the case were no hydrogen originally present in the mixture. Recently the writer in an unpublished research on the division of oxygen between methane and hydrogen, in which mixtures corresponding to $CH_4+O_2+xH_2$ ($x=2$, 4, 6, or 8) have been exploded at high initial pressures, has proved that with $x=2$ upwards of 95 per cent of the oxygen initially reacts with the hydrocarbon, and less than 5 per cent of it goes to the hydrogen. Moreover, the proportion of the oxygen which goes to the hydrogen has been found to increase according to the second power of x, a circumstance which suggests that the combustion of hydrogen involves the trimolecular reaction $2H_2+O_2=2H_2O$, and not the initial formation of hydrogen peroxide, as some have supposed. A similar series of experiments with mixtures CH_4+O_2+xCO have proved that the affinity of carbon monoxide for oxygen is even less than that of hydrogen, and that the proportion of oxygen going to it increases as approximately the first power of x.

These observations have an important bearing on the chemistry of flames; hitherto hydrogen has been considered as one of the most combustible of gases, but in reality it is very much less so than hydrocarbons. Indeed, so overwhelmingly great is the affinity of a hydrocarbon for oxygen, as compared with the affinities of either hydrogen or carbon monoxide or with its own tendency to decompose, that the initial stage of its combustion probably takes precedence of all other chemical phenomena in flames. This is certainly true of the propagation of flame through a homogeneous explosive mixture of hydrocarbon and oxygen. In the special case of a steam of hydrocarbon burning in air, partial decomposition may possibly occur in the innermost regions of the flame, where the supply of oxygen is very limited, before actual combustion begins. But in general, whenever the hydrocarbon and oxygen meet at high temperatures, their mutual affinities will prove superior to any disruptive force whigh might otherwise break down the hydrocarbon. It is probably not so much the original hydrocarbon as its hydroxylated molecule which decomposes in ordinary flames. Be this, however, as it may, the experimental evidence does not warrant the view, so often encountered in scientific literature, that hydrocarbons are resolved into their elements prior to being burnt.

(Note.—No attempt has been made in this report to discuss in any detail the experimental evidence on which the new theory of hydrocarbon combustion is based; the reader is referred to the series of papers published by the writer and his pupils (R. V. Wheeler, W. E. Stockings, G. W. Andrew, Julian Drugman, and H. L. Smith) in the *Trans. Chem. Soc.*, 1902, lxxxi., 535; 1903, lxxxiii., 1074; 1904, lxxxv., 693, 1637; 1905, lxxxvii., 1910, 1232; 1906, lxxxix., 652, 660, 939, 1614).

(To be continued).

EFFLORESCENCE OF WASHING SODA CRYSTALS.

By ALEXANDER CHARLES CUMMING.

In the course of some recent work on the hydrates of sodium carbonate attention was directed to a lecture specimen of what had been large crystals of washing soda, but which appeared to have effloresced. The crystals have been for at least twenty years in a glass case with a wooden floor. The case fits closely, but is by no means air-tight. As it was thought that the crystals were a lower hydrate than the decahydrate, the percentage of sodium was calculated from the loss of weight on ignition, and found to be 30·75 per cent. This would agree roughly with the hydrate, $Na_2CO_3.3H_2O$ (calculated per cent of sodium = 28·8). A hydrate of this composition has been described, but other work pointed to the non-existence of any hydrates except those with 1, 7, and 10 molecules of water of crystallisation (*Trans. Chem. Soc.*, 1910, xcvii., 593). Mr. J. B. Robertson, M.A., kindly analysed another portion by several methods, and his results indicate that the substance has been converted into sodium sesquicarbonate.

	Na, per cent.	CO_2, per cent.
Found	30·6	38·2
Calculated for—		
$Na_2CO_3.NaHCO_3.2H_2O$ ..	30·5	38·9
$Na_2CO_3.10H_2O$	16·1	15·4
$NaHCO_3$	27·4	52·4

These results show that the substance is now almost pure sesquicarbonate. It is remarkable that the conversion should be so complete, as the glass case fits fairly closely, and the specimen weighs several pounds. Sodium sesquicarbonate occurs in nature as the mineral known as *trona*, which is described in modern text-books of mineralogy as having the composition shown by the formula $Na_2CO_3.NaHCO_3.2H_2O$, but which is described in some text-books of inorganic chemistry as $Na_2CO_3.2NaHCO_3.2H_2O$.

Systematic investigation of the hydrates of sodium carbonate by several investigators has revealed no evidence of a trihydrate, and it seems probable that a specimen of the sesquicarbonate was mistaken for sodium carbonate trihydrate. The loss of weight on ignition of the sesquicarbonate, if calculated as due entirely to water, would lead to the formula for the trihydrate.

It may be suggested also that crystals described as $Na_2CO_3.4H_2O$ were really sodium bicarbonate. The residue left after heating $NaHCO_3=63·2$ per cent, and the residue from $Na_2CO_3.4H_2O$ would be 60·9 per cent. The chemical evidence is against the existence of these two hydrates, but they are still given in some chemical dictionaries.

Chemistry Department,
University of Edinburgh.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 8th, 1910.

Mr. A. B. KEMPE, Treasurer and Vice-President, in the Chair.

THE CHAIRMAN announced that the President had appointed as Vice-Presidents:—The Treasurer (Mr. A. B. Kempe), the Duke of Northumberland, Mr. L. Fletcher, Dr. W. H. Gaskell, Prof. J. H. Poynting.

Papers were read as follows: –

"*Colour Blindness and the Trichromatic Theory of Colour Vision.* Part II.—*Incomplete Red or Green Blindness.*" By Sir W. de W. ABNEY, K.C.B., F.R.S.

In this paper the author continues the subject of the trichromatic theory of colour vision and colour blindness. In Part I. he treated of complete colour blindness, and in this paper, Part II., he treats of incomplete colour blindness. He shows how the amount of incompleteness can be accurately determined from the luminosity curve of a colour-blind person both red and green blind. He also shows that the amount of incompleteness can be determined from observations made by the red or green blind at any part of the spectrum, if someone with normal vision makes observations at the same place using unchanged white light for the comparison. Incidentally he shows that the three sensation components of the different colours of the spectrum, as determined by himself, are verified by the results; and that the trichromatic theory fully accounts for all cases of incomplete colour blindness which he has measured.

"*Sensibility of the Eye to Variations of Wave-length in the Yellow Region of the Spectrum.*" By LORD RAYLEIGH, O.M., F.R.S.

"*Trypanosome Diseases of Domestic Animals in Uganda.* IV.—Trypanosoma uniforme, *sp. nov.*" By Colonel Sir D. BRUCE, C.B., F.R.S., and others.

"*Trypanosome Diseases of Domestic Animals in Uganda.* V.—Trypanosoma nanum (*Laveran*)." By Colonel Sir D. BRUCE, C.B., F.R.S., and others.

"*Some Enumerative Studies on Malarial Fever.*" By Major RONALD ROSS, F.R.S., and DAVID THOMSON, M.B., Ch.B., D.P.H.

The object of these researches was to make a minute co-ordinated study of cases of malarial infection occurring in the Tropical Ward of the Royal Southern Hospital at Liverpool. The first care of the authors was to elaborate a method by which the number of parasites could be correctly counted, and the one which they adopted was to make a measured quantity of blood into a de-hæmoglobinised thick-film, and then to count the organisms contained in it.

Almost daily estimates of the number of parasites, with frequent estimates of the leucocytes, the hæmoglobin, and the excreted urobilin, were made since the beginning of this year in twenty-four cases of *Plasmodium falciparum*, eight cases of *P. vivax*, and one case of *P. malariæ* and *P. falciparum*.

Correlation with minor deviations was found between the number of asexual parasites present and the degree of fever. If the asexual forms did not number more than several hundreds per c.mm. they were not numerous enough in these cases to produce fever. The asexual forms do not disappear between relapses as usually thought, but tend to diminish.

It is roughly estimated from these cases that quinine reduces the asexual forms by 50 to 80 per cent.

"*Hæmoglobin Metabolism in Malarial Fever.*" (Preliminary Note). By G. C. E. SIMPSON, B.A., M.B.

In the pyrexia of malaria there is a marked fall in the hæmoglobin of the blood, and further investigation of this question was undertaken in the hope that it might throw light on the relationship of malaria and blackwater fever.

In benign tertian malaria a slightly increased output of urinary urobilin occurs; in malignant tertian malaria, a greater increase; and in the malignant form, marked urobilinuria was sometimes found.

More urobilin is excreted in the fæces than in the urine, a fact which has been largely neglected by previous observers.

In benign malaria fæcal urobilin is excreted in amounts comparable to those in other pyrexial diseases; in malignant malaria a higher output is the rule, and it may represent as much as 25 per cent of the total blood. This shows that the hæmoglobinometer readings record an actual destruction of hæmoglobin. The number of corpuscles destroyed is larger than the number infected by parasites.

It would appear that in malignant tertian malaria the removal of freed hæmoglobin by the liver prevents hæmoglobinæmia of sufficient grade to produce hæmoglobinuria. A remarkable excretion of urobilin was found in a case of blackwater fever, representing the destruction of an amount of hæmoglobin equal to the whole of the circulating blood, the amount of hæmoglobin passed unchanged in the urine being negligible in comparison. Hæmoglobinuria in this case was not due to failure of the normal mechanisms to deal with an amount of hæmoglobin such as is set free in ordinary malaria, but to a slight overflow of hæmoglobin through the kidneys owing to the exceptional amount of hæmolysis.

The daily findings are included in the paper, "Some Enumerative Studies on Malarial Fever," by Ross and Thomson.

"*Case of Sleeping Sickness studied by precise Enumerative Methods: Further Observations.*" By Major RONALD ROSS, C.B., F.R.S., and DAVID THOMSON, M.B., Ch.B., D.P.H.

1. The trypanosome cycle recorded by us in our previous paper continued till the patient's death.

2. The amount of fever was greater during the trypanosome increase.

3. The total leucocytes increased coincidently with the trypanosome increase. The mononuclears increased relatively more than the polymorphonuclears. During the trypanosome fall the leucocytes continued to increase in number. The number then decreased rapidly to normal and under when the trypanosomes again commenced to increase. A very marked mononuclear increase, coincident with a decrease of trypanosomes, was accompanied by a remarkable clinical improvement.

4. *Drug Treatment:* Atoxyl in small doses, 2 to 4 grains, showed no appreciable trypanocidal action. Quinine and methylene blue in large doses had no appreciable trypanocidal action.

5. Subcutaneous injection of vaccines of trypanosomes obtained from heavily infected rats seems to cause a premature rise in number of the patient's trypanosomes; the effect depended upon the time of injection in relation to the cycle.

6. Subcutaneous injection of leucocytic extract caused a marked leucocytosis on the day after the injection, and on one occasion this leucocyte increase was coincident with a marked clinical improvement.

Conclusions.

1. The increase of trypanosomes is due to their active multiplication depending on the following conditions:—

(*a*) The liberation of a reproductive stimulant from the dead trypanosomes of the previous fall.

(*b*) The small number of leucocytes, especially mononuclears.

(*c*) The habituation of the trypanosomes to their antibodies.

(*d*) The absence or diminution of antibodies.

2. The decrease of trypanosomes is due to their rapid

death, and to a cessation of multiplication depending on the following conditions :—

(*a*) The large increase of leucocytes, especially of mononuclears.

(*b*) The formation of antibodies in the serum.

3. The trypanosomes remaining between the rises are resistant forms.

4. Extracts of dead cells would appear to stimulate the corresponding live cells to multiply or divide.

"*Enumerative Studies on* Trypanosoma gambiense *and* Trypanosoma rhodesiense *in Rats, Guinea-pigs, and Rabbits ; Periodic Variations Disclosed.*" By H. B. Fantham, D.Sc., B.A., and J. G. Thomson, M.A., M.B., Ch.B.

The main points of the paper may be thus summarised : —

1. The strains of trypanosomes used in these investigations were :—

(*a*) *T. gambiense*, old laboratory strain.

(*b*) *T. rhodesiense* (Stephens and Fantham), from a patient suffering from Sleeping Sickness in Rhodesia.

2. Rats, guinea-pigs, and rabbits were inoculated with a definite number of trypanosomes, and daily counts were made of the parasites in the peripheral blood of the animals.

3. Periodic variation was found in all these animals comparable to that discovered by R. Ross and D. Thomson in the blood of the Sleeping Sickness patient.

4. Rats inoculated with each strain showed either a periodic increase or a continuous rise in the numbers of parasites.

5. The average life of rats inoculated with *T. rhodesiense* was 11·3 days; with *T. gambiense*, 13·8 days.

6. The average incubation period in rats in the case of *T. rhodesiense* was 2·9 days ; in *T. gambiense*, 4·4 days. The average weights of the animals and the average number of parasites inoculated were approximately the same in the two strains.

7. In rats infected with *T. rhodesiense*, the period between the crests of the graph was 3 to 4 days, while in *T. gambiense* this period was 4 to 6 days.

8. In guinea-pigs the typanosomiasis tended to run a chronic course, but the life of animals infected with *T. rhodesiense* was shorter. The period between the crests of the graph in both strains was longer than in rats—namely, 5 to 8 days.

9. Rabbits inoculated with *T. rhodesiense* also exhibit periodic variation.

10. The periodicity is explained by (*a*) variations in resistance on the part of the host, accompanied by (*b*) the formation of latent bodies by the trypanosomes in the internal organs of the host during fall in numbers of the parasites in the peripheral blood.

"*Life-History of* Trypanosoma gambiense *and* Trypanosoma rhodesiense *as seen in Rats and Guinea-pigs.*" By H. B. Fantham, D.Sc., B.A., A.R.C.S.

The main points in the paper may be summarised thus :

1. The researches were undertaken to investigate the parasitological aspect of the numerical cyclical development found by R. Ross and D. Thomson in the trypanosome of a patient suffering from Sleeping Sickness contracted in Rhodesia. Rats and guinea-pigs inoculated with *T. rhodesiense* and with *T. gambiense* were killed at various stages of infection and their internal organs examined, controls being used.

2. The formation of a non-flagellate, latent, or rounded body from a trypanosome was observed in life, much of the cytoplasm and the flagellum of the flagellate being cast off.

3. Non-flagellate bodies were seen to grow into flagellate trypanosomes when placed in fresh warm uninfected blood.

4. The latent or non-flagellate stages are formed at or near the time when the trypanosomes are most numerous in the peripheral blood.

5. The latent bodies are relatively numerous in the internal organs when the flagellates are few in the peripheral blood of the host.

6. The formation of latent bodies takes place especially in the lungs. The latent bodies collect in the spleen and bone-marrow, as stated by Salvin-Moore and Breinl.

7. Latent bodies from the spleen of an infected rat inoculated into another rat produced trypanosomiasis.

8. The latent bodies are the post-flagellate stages of one generation of trypanosomes and the pre-flagellate stages of the succeeding generation.

9. There is a life-cycle of *T. gambiense* and of *T. rhodesiense* in vertebrate hosts. (Compare *Crithidia* and *Herpetomonas* in invertebrates).

10. The occurrence of latent bodies explains the recurrence of trypanosomiasis in hosts when it has apparently died out.

11. Mutual action and reaction of the host and the parasite lead to the formation of rounded bodies, which are relatively resistant.

12. Some flagellate trypanosomes do not form latent bodies, but degenerate. Some latent bodies die, and do not flagellate.

"*Experiments on the Treatment of Animals infected with Trypanosomes by means of Atoxyl, Vaccines, Cold, X-Rays, and Leucocytic Extract ; Enumerative Methods Employed.*" By Major R. Ross, C.B., F.R.S., and J. G. Thomson, M.A., M.B., Ch.B.

In all the animals used in these experiments regular daily counts were made of the parasites in the peripheral blood, by means of thick film method.

1. Small repeated doses of atoxyl prolonged the lives of rats infected with the Rhodesian strain of trypanosomes, but failed to have any trypanocidal action, as was demonstrated by the fact that the parasites increased rapidly and showed very active division.

2. We venture to suggest that small doses of atoxyl actually stimulated the trypanosomes of this strain to divide, and that the drug is also a tonic to the body cells of the host.

3. Large doses of atoxyl are trypanocidal, but the parasites form resistant bodies and cure is only temporary. The dose required to approach as near lethal as possible, and even then a cure was not obtained in the Rhodesian strain.

4. Vaccine treatment gave indefinite results and insufficient experiments prevent definite conclusions being formed. The life of one rat seemed to be prolonged when the vaccine was administered in doses of 10,000,000 trypanosomes, with an interval between the doses. We suggest that the time of administration, the amount given, and the interval between the doses, are all of importance, and further work is being carried out.

5. Animals suffering from trypanosomiasis had the incubation period delayed, and their lives prolonged in the cold.

6. X-rays had no trypanocidal action, but the life of the animal may have been prolonged.

7. Leucocytic extract gave indefinite results.

"*Sound Vibrations of Very High Frequency produced by Electric Sparks.*" By Albert Campbell, B.A., and D. W. Dye, B.Sc.

CHEMICAL SOCIETY.

Ordinary Meeting, November 17th, 1910.

Prof. Harold B. Dixon, M.A., Ph.D., F.R.S., President, in the Chair.

Messrs. Harry Farrands and Percy G. Ward were formally admitted Fellows of the Society.

The President read the following letter :—

Home Office, Whitehall, July 6th, 1910.

Sir,—I am commanded by the King to convey to you hereby his Majesty's thanks for the loyal and dutiful Address of the President, Council, and Fellows of the Chemical Society, expressing their sympathy with his

Majesty on the occasion of the lamented death of his late Majesty King Edward the Seventh, and congratulation on his Majesty's accession to the throne.—I am, Sir, your obedient servant,

WINSTON S. CHURCHILL.

The Hon. Secretary, The Chemical Society,
Burlington House, W.

The PRESIDENT stated that he had received the following letter from Prof. Körner:—

Milano li 8 Ottobre, 1910.

HOCHGEEHRTER HERR PRÄSIDENT,—Die Feier, welche Freunde und Collegen gelegentlich der 70 ten Wiederkehr meines Geburtstages (20 April, 1839) veranstaltet haben und die erst am 15. Mai dieses Jahres zur Ausführung kommen konnte, hat eine ganz besondere Zierde empfangen durch die nur allzu schmeichelhafte Anerkennung, welche die Chemische Gesellschaft zu London in prächtig ausgestatteter Adresse meinem Wirken als Lehrer und Forscher hat zu Theil werden lassen. Ich brauche Ihnen wohl nicht zu sagen, wie sehr mich diese wohlwollende Beurtheilung erfreut hat und wie hoch ich die Ehre schätze, die ich dadurch erhalten habe.

Ich bitte die Chemische Gesellschaft, und zugleich ihren Präsidenten, Herrn Professor Harold B. Dixon, meinen wärmsten Dank für diese Ehrung entgegenzunehmen und verbleibe Herr Präsident, mit ausgezeichneter Hochachtung. —Ihr, sehr ergebener,

Prof. W. KÖRNER.

Herrn Professor Harold B. Dixon, F.R.S.,
Präsident der Chemischen Gesellschaft zu London.

The PRESIDENT announced that the Eighth International Congress of Applied Chemistry would be held in Washington and in New York in September, 1912.

He also announced that a letter had been received from the Board of Trade drawing the attention of Fellows of the Society to the forthcoming International Exhibition to be held in Turin next year. A Royal Commission under the chairmanship of the Earl of Lytton is now engaged in organising exhibits illustrative of British Industry and Agriculture. The formation of a Scientific Section in the Exhibition is proposed.

Certificates were read for the first time in favour of Messrs. Edward Anderson, Hill View House, Waun Wen Road, Swansea; Walter Norman Burbridge, Uplands, Foxley Lane, Purley; John Fisher Carmichael, B.Sc., Tower Building, Liverpool; Henry George Alan Harding, Darling Street, Chatswood, Sydney, N.S.W.; William Alfred Jenkin, 6, Bella Vista, Rio Tinto, Spain; John Watterson Miller, Lynwood, Cantilupe Street, Hereford; Walter Roman Moore, 55, Gloucester Street, Norwich; Frank Henry Plews, 28, Gellatly Road, St. Catherine's Park, S.E.; Henry Stanley Raper, 599, Spadina Avenue, Toronto; George Douglas Summers, Easington Lodge, Stroughton, Ipswich.

Certificates have been authorised by the Council for presentation to Ballot under By-law I. (3) in favour of Messrs. Charles Crichton, Afrikander Mine, Klerksdorp, Transvaal; Marshall Perley Cram, A.M., Ph.D., Brunswick, Maine, U.S.A.; Count Arnaud de Gramont, Rue de l'Universite 49, Paris; Alleyne Leechman, B.A., 55, Main Street, Georgetown, British Guiana; John Fleming Culun Brown Vance, 947, Richard Street, Vancouver, B.C.

Of the following papers, those marked * were read:—

*300. "*Preparation of Secondary Amines from Carboxylic Acids.* Part I. *Preparation of Heptadecylaniline, Pentadecylaniline, and Tridecylaniline.*" By HENRY RONDEL LE SUEUR.

Heptadecylaniline, $C_{27}H_{35}\cdot NH\cdot C_6H_5$, is readily obtained by heating α-anilinostearic acid, $C_{16}H_{33}\cdot CH(NHPh)\cdot CO_2H$, to considerably above its melting-point, whereby it loses carbon dioxide:—

$$C_{16}H_{33}\cdot CH(NHPh)\cdot CO_2H \rightarrow C_{17}H_{35}\cdot NH\cdot C_6H_5.$$

The compound crystallises from alcohol in needles, melting at 42—43°, and boils at 285—286°/35 mm. Its *hydrochloride* melts at 99—100°.

Pentadecylaniline, $C_{15}H_{31}\cdot NH\cdot C_6H_5$, similarly obtained from α-anilinopalmitic acid, $C_{14}H_{29}\cdot CH(NHPh)\cdot CO_2H$, melts at 34—35°, and boils at 271°/40 mm. Its *hydrochloride* melts at 97·5°.

Tridecylaniline, $C_{13}H_{27}\cdot NH\cdot C_6H_5$, obtained from α-anilinomyristic acid, $C_{12}H_{25}\cdot CH(NHPh)\cdot CO_2H$, melts at 23—24°, and boils at 251°/35 mm.

The author is now engaged in the investigation of the application of the above reaction to the preparation of secondary amines, and more particularly of substituted anilines and naphthylamines.

*301. "*The Wet Oxidation of Metals.* Part I. *The Rusting of Iron.*" By BERTRAM LAMBERT and JAMES CAMPBELL THOMSON.

The work published up to the present time on the subject of the rusting of iron cannot be held to prove the fact that pure iron will not undergo visible oxidation in contact with pure water and pure oxygen. In almost all previous investigations, commercial iron of the highest obtainable degree of purity has been used, but, from a chemical point of view, the impurities contained in the iron must have been considerable, even in the most favourable circumstances.

The authors have shown that pure iron, prepared from pure ferric nitrate by igniting to form the oxide, and subsequently reducing in a pure iridium boat in a current of pure hydrogen, does not show visible oxidation after long exposure to pure water and pure oxygen.

The experiments were carried out in vessels of clear fused silica, the water was distilled in a vacuum from a solution of barium hydroxide, and the oxygen was prepared by the electrolysis of a solution of highly purified barium hydroxide.

It has been shown, further, that iron containing a slight trace of impurity will undergo oxidation under the same conditions, even when there is no possibility of an acid substance being either present or formed during the reaction.

DISCUSSION.

The PRESIDENT asked whether Mr. Lambert had taken any measures to free the electrolytic oxygen from diffused hydrogen before bringing it into contact with the iron. He expressed his conviction that Mr. Lambert had amply proved that iron purified by the method described was not oxidised in contact with water and oxygen.

Sir W. RAMSAY suggested that stopcocks, greased at the ends with grease and lubricated with phosphoric oxide in the middle round the bore, held tight. He also pointed out that silica dissolves to some extent in water, and that an acid solution (?) might be formed; but pure iron is not attacked by strong acids, and *à priori* would not be attacked by water.

Prof. ARMSTRONG expressed the opinion that the results brought forward in no way affected the conclusions arrived at by Moody and confirmed by Friend. It was to be expected, on theoretical grounds, that iron would not be attacked to any appreciable extent if highly purified; action should take place only in presence of a relatively electronegative conductor, such as platinum; in point of fact, the results arrived at were such as should be arrived at, and were in no way surprising. That rusting would take place under the conditions described if impure iron were used was also to expected; in carrying out the experiments, apparently, no proper care had been taken to exclude carbon dioxide; it was well known that this gas was obstinately retained by glass surfaces, and could not be removed by mere evacuation. The speaker also suggested that the term "purified" should be used instead of "pure" throughout the communication.

Mr. ARNOLD PHILIP asked whether the authors had tried the action of pure oxygen and water on a mixture of two portions of the same sample of pure iron, one of which portions had been strained mechanically; for instance, by hammering, and the other portion being retained in an

unstrained condition. It occurred to him that such a mixture might behave similarly to the mixture of pure iron with traces of platinum described by the authors.

Mr. Lambert, in reply to the President, said that the construction of the electrolytic cell precluded the possibility of the diffusion of hydrogen into the oxygen ; any hydrogen which diffused back from the cathode must escape into the reservoir of the cell.

In reply to Sir W. Ramsay, he stated his opinion that a glass stopcock, treated as suggested, would not prevent a slow leakage of gas round the barrel of the stopcock if it were lubricated with phosphoric acid, and if the conditions were such that there was a wet gas on one side of the stopcock and a high vacuum on the other side ; in time the lubricant must be partly washed away. There was no question of leakage from the outside of the stopcock, since it was mercury-sealed.

In reply to Prof. Armstrong, he said that he could not agree that the experiments did not affect the conclusions arrived at by Moody. Moody's contention was that pure iron would only undergo oxidation in contact with water and oxygen when carbon dioxide, or some such acid gas, is present ; that, in the absence of this last condition, pure iron will not rust. Moody's experiments were conducted with impure iron and air which was only freed from acid gases ; the conditions of experiment were further complicated by his method of treating the iron, so that no simple conclusion could be drawn from his experiments, and certainly none which could be applied to pure iron. Mr. Lambert said that experiments (an account of which was shortly to be presented to the Society) which had been carried out since this paper had been submitted showed that pure iron, made according to the method described in the paper, could be exposed to water and ordinary air without undergoing oxidation—a result which showed that Moody's contention was not true.

With regard to the use of the term "pure," such a term could only be used with a relative meaning in chemistry.

Experiments on the lines of Mr. Philip's suggestion had not been carried out.

302. "*The Colour and Constitution of Diazonium Salts.* Part III. *The Diazo-derivatives of* 2 : 7-*Naphthylenediamine.*" By Gilbert T. Morgan and Frances M. G. Micklethwait.

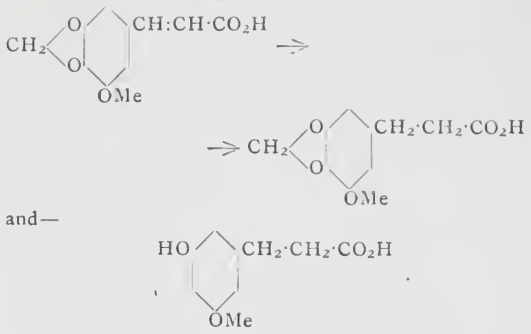
Both the amino-groups of 2 : 7-naphthylenediamine can be diazotised by operating with sodium nitrite or nitrosyl sulphate in moderately concentrated sulphuric acid. The addition of ether and alcohol to this solution caused the precipitation of *naphthalene*-2 : 7-*bisdiazonium sulphate*, $C_{10}H_6(N_2{\cdot}HSO_4)_2,\frac{1}{2}C_2H_5{\cdot}OH$ (compare Kaufler and Karrer, *Ber.*, 1907, xl., 3263). This salt was utilised in the preparation of *naphthalene*-2 : 7-*bisdiazonium platinichloride*, $C_{10}H_6(N_2)_2PtCl_6.2H_2O$; *aurichloride*, $C_{10}H_6(N_2{\cdot}AuCl_4)$; and *dichromate*, $C_{10}H_6(N_2)_2{:}Cr_2O_7$ These bisdiazonium salts are decomposed quantitatively by sodium azide, yielding 2 : 7-*bistriazonaphthalene* (*naphthylene*-2 : 7-*bisazoimide*), $N_3{\cdot}C_{10}H_6{\cdot}N_3$ (m. p. 98°), and when subjected to the Sandmeyer reaction in presence of hydrochloric acid they furnish 2 : 7-dichloronaphthalene (m. p. 114°).

These results were employed in the discussion of the authors' views on the constitution of diazonium salts.

303. "*Action of Sodium Amalgam on Methylene Ethers.*" By Arthur Henry Salway.

The author has investigated the action of sodium amalgam on 3-methoxy-4 : 5-methylenedioxycinnamic acid, and has found that the normal reaction is accompanied by a secondary change involving the disruption of the methylene dioxy-complex and the formation of β-5-hydroxy-3-methoxyphenylpropionic acid, according to the accompanying scheme.

A similar change was shown to be general in the case of those aromatic methylene ethers which contain an aliphatic side-chain unsaturated in the αβ-position with respect to the benzene nucleus,



304. "*The Homogeneous Decomposition of Ozone in the presence of Oxygen and other Gases.*" By David Leonard Chapman and Herbert Edwin Jones.

The authors have continued the work of Clarke and Chapman, in which it was shown that the decomposition of ozone in glass vessels of a sufficient size is a homogeneous change.

The results obtained have demonstrated that :—

(*a*) Oxygen, nitrogen, carbon dioxide, and possibly water-vapour have no effect on the rate of decomposition of ozone ; that is, the rate of decomposition of ozone in the presence of these gases is a function of the concentration of the ozone only.

(*b*) Nitrogen peroxide (Andrews) and chlorine accelerate in a marked degree the decomposition of the gas.

(*c*) If the order of the change can be represented exactly by an integral ordinal number, that number is the second.

305. "*The Addition of Bromine to Unsaturated Compounds.*" (Part II.). By John Joseph Sudborough and John Thomas.

The addition of bromine to the following acids in carbon tetrachloride solution at 15° has been studied :—Cinnamylideneacetic and *allo*cinnamylideneacetic acids, sorbic and hydrosorbic acids. the three dihydrocinnamylideneacetic acids, and crotonic, angelic, tiglic, β-dimethylacrylic, and trimethylacrylic acids.

The results confirm the conclusion already drawn, namely, that acids with an olefine linking in the αβ-position react with bromine much less readily than isomeric βγ- or γδ-acids.

The presence of several methyl groups in the acrylic acid molecule facilitates the addition of bromine to the acid.

306. "*Intermolecular Condensation of Aromatic Sulphinic Acids.*" (Part I.). By Thomas Percy Hilditch.

It is found that when the chlorides of aromatic sulphinic acids are heated to 60—100°, or kept in cold concentrated sulphuric acid, or when the free sulphinic acids are left for some time in sulphuric acid solution, a decomposition takes place, the nature of which is chiefly determined by the substituents in the aromatic nucleus. Thus, in general, those acids in which the para-position with respect to the sulphinyl group is unsubstituted give varying proportions of insoluble compounds of high melting-points and of the corresponding disulphoxide, whilst if that position is occupied, small amounts of disulphoxide only are formed. With the heated sulphinyl chlorides, disulphides may appear with, or in place of, the disulphoxides.

The insoluble derivatives possess the composition :—R $C_6H_3{:}S_2O_2{:}C_6H_3{\cdot}R$, and were found to be closely connected with the insoluble by-products nearly always formed in syntheses of thianthrene. It has further been proved that the insoluble product thus obtained from benzenesulphinic acid is analogous to the "*iso*thianthrene" described by Genvresse, and that, since *p*-dichlor benzene and benzene-*p*-disulphonyl chloride result from the action of phosphorus pentachloride on the compound, the sulphur atoms are united to each benzenoid residue through the para-carbon atoms. It is accordingly suggested that the

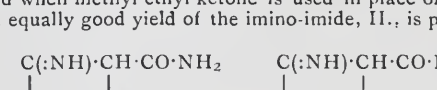
term "*iso*thianthrene" be replaced by the more appropriate "parathianthrene."

On account of the sparing solubility and volatility of these derivatives, it has been impossible to determine the molecular complexity of the parathianthrenes, but further proof of their para-configuration lies in their non-appearance from any para-substituted sulphinic acids.

307. "*Formation of a Six-membered Ring through the Agency of the Imino-group.*" (Preliminary Note). By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE.

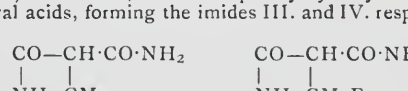
It is found that an open chain of five carbon atoms and one nitrogen atom readily passes into the six-membered ring through the agency of the imino-group.

Thus, when acetone is condensed with cyanoacetamide in the presence of piperidine or sodium hydroxide, an almost quantitative yield of the imino-imide, I., is formed, and when methyl ethyl ketone is used in place of acetone an equally good yield of the imino-imide, II., is produced.



I. II.

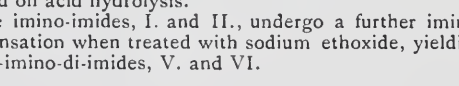
These substances are tautomeric imino-amino- (ketimino-enamic) derivatives, which are quickly hydrolysed by dilute mineral acids, forming the imides III. and IV. respectively.



III. IV.

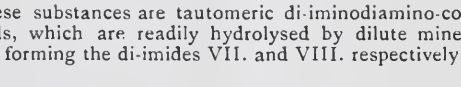
Either from the imino-imides or from the imides a quantitative yield of the $\beta\beta$-substituted glutaric acid is formed on acid hydrolysis.

The imino-imides, I. and II., undergo a further imino-condensation when treated with sodium ethoxide, yielding the di-imino-di-imides, V. and VI.



V. VI.

These substances are tautomeric di-iminodiamino-compounds, which are readily hydrolysed by dilute mineral acids, forming the di-imides VII. and VIII. respectively.

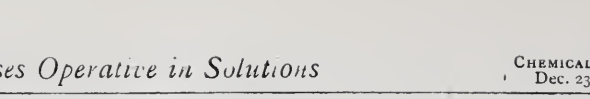


VII. VIII

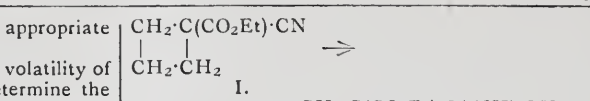
These compounds are also converted into the corresponding dialkylglutaric acids on complete acid hydrolysis.

308. "*An instance Illustrating the Stability of the Four Carbon Ring.*" By ARTHUR FRED CAMPBELL and JOCELYN FIELD THORPE.

It was shown that under the same experimental condition that produce ethyl $\alpha\alpha$-dicyanoadipate from ethyl 1-cyano*cyclo*propane-1-carboxylate and ethyl cyanoacetate, the corresponding *cyclo*butane derivative, ethyl 1-cyano-*cyclo*butane-1-carboxylate, I., is converted into an imino-compound, II.



I.



II.

The derivatives of this imino-compound were described.

309. "*Narcisine: An Alkaloid from the Bulb of the Common Daffodil* (Narcissus Pseudonarcissus)." By ARTHUR JAMES EWINS.

A new alkaloid, *narcissine*, has been isolated from the bulb of the common daffodil (*Narcissus pseudonarcissus*). It has been shown to possess the formula $C_{16}H_{17}O_4N$, melts at 266—267°, and is lævorotatory ($[\alpha]_D$ 95·8°). It contains no methoxy-groups, and is characterised by great stability.

The *hydrochloride*, $C_{16}H_{17}O_4N,HCl$, was also described.

310. "*Preparation of Ammonium Nitrite by the Sublimation in a Vacuum of a Mixture of Ammonium Chloride and Alkali Nitrites.*" By PANCHANAN NEOGI and BIRENDRA BHUSAN ADHICARY.

The authors have prepared in fairly large amount the unstable compound, ammonium nitrite, by evaporating and subliming in a vacuum a concentrated solution of ammonium chloride and alkali nitrites. The method of preparation of the compound, its properties, and the results of vapour density determinations by Hofmann's method at different temperatures were described.

311. "*The Action of Halogens on Mercuricamphor Compounds.*" By JAMES ERNEST MARSH.

Di-iodocamphor is formed by the action of iodine on each of the three mercuricamphor compounds, $C_{10}H_{14}O,Hg_2I_2$, $(C_{10}H_{14}O)_3Hg_4I_2$, and $(C_{10}H_{14}O)_4Hg_5I_2$. Di-iodocamphor is decomposed in solution by the oxygen of the air with liberation of iodine and formation of camphorquinone. Di-iodocamphor and the mercuricamphors are thus shown to be $\alpha\alpha'$-derivatives of camphor. The action of bromine on dimercuricamphor compounds and on di-iodocamphor gives $\alpha\alpha'$-dibromocamphor.

312. "*The Absorption Spectra of Various Diketopyrroline Compounds.*" By JOHN EDWARD PURVIS.

The results of this investigation show that—(1) the diketonic structure gives rise to the production of a well-marked colour and absorption; (2) the introduction of a methyl or a propyl group in an aromatic side-chain produces no fundamental change in the colour or the absorption; (3) the introduction of an anisyl or a piperonyl group in an aromatic side-chain does not fundamentally alter the colour or the corresponding absorption, but another more refrangible band is produced characteristic of each type of radicle; (4) the replacement of oxygen in a ketonic group by phenylhydrazine produces a change in the colour and the absorption, so that two bands are developed, the less refrangible one being the stronger; (5) the replacement of both oxygen atoms and the establishment of a phenazine ring is marked by a further change in the colour from red to yellow, a decrease in the strength of the less refrangible band, and an increase in the strength of the more refrangible one; (6) the increased weighting of the molecule shifts the positions of general absorption towards the more refrangible regions.

313. "*Studies of the Processes Operative in Solutions.* Part XII. *The Apparent Hydration Values of Acid-Systems and of Salts Deduced from a Study of the Hydrolytic Activities of Acids.*" By FREDERICK PALLISER WORLEY.

An account was given of an extended series of observations on the behaviour of cane-sugar in aqueous solutions towards chlorhydric and nitric acids, and of the influence of salts on the rate of change. The results were discussed with reference especially to the determination of the apparent hydration value of the solutes.

314. "*Studies of the Processes Operative in Solutions.* Part XIII. *The Depression of the Hydrolytic Activity of Acids by Paraffin-id Alcohols and Acids.*" By Henry E. Armstrong and Frederick Palliser Worley.

It was shown that the depressant influence increases as the molecular weight of the depressant increases.

315. "*Studies of the Processes Operative in Solutions.* Part XIV. *The Determinations of Apparent Hydration Values by means of Raffinose.*" By Walter Hamis Glover.

The values arrived at when raffinose is hydrolysed in presence of salts were shown to be practically identical with those obtained on using cane-sugar as hydrolyte.

316 "*Studies of the Processes Operative in Solutions.* Part XV. *The Changes effected by the Reciprocal Interference of Sugar (and Glucosides) and Salts in Aqueous Solutions.*" By Walter Hamis Glover.

This communication is an extension of the work described in Part X. (*Proc. Roy. Soc.*, A, 1908, lxxxi., 117), in which the effect of cane-sugar on the rotatory power and electrical conductivity of solutions of various salts was considered. The sugars studied are raffinose, together with melibiose, milk-sugar, and α- and β-methyl-glucoside.

317. "*Studies of the Processes Operative in Solutions.* Part XVI. *The Determination of Optical Rotatory Power.*" By Frederick Palliser Worley and Walter Hamis Glover.

Various refinements were described that have been made use of in carrying out the determinations described in Parts XII. XIV.

318. "*Studies of the Processes Operative in Solutions.* Part XVII. *The Relative Efficiencies of Acids as Deduced from their Conductivities and Hydrolytic Activities.*" (II.). By Henry E. Armstrong and Edward Wheeler.

The acids studied are chlorhydric, bromhydric, and iodhydric—the acids formed by the dissolution of the three hydrides HCl, HBr, HI.

319. "*Studies of the Processes Operative in Solutions.* Part XVIII. *The Depression of Electrical Conductivity by Non-electrolytes.*" By Henry E. Armstrong and David Crothers.

Results were given showing the effects produced at 0° and 25°. Attention was particularly directed to the remarkable manner in which the depressant effect increases as the molecular weight of the depressant increases.

320. "*Studies of the Processes Operative in Solutions.* Part XIX. *The Complexity of the Phenomena afforded by Solutions: a Retrospect.*" By Henry E. Armstrong.

A summary was given of the results recorded in previous communications of the series, and their bearing on the problems afforded by solutions was discussed.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, December 7th, 1910.

Mr. A. E. Ekins, Vice-President, in the Chair.

Messrs. Gunner Jorgensen and Frederick Farey Shelley were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. Ronald Leslie Collett, Little Dawley, Hayes, Middlesex; William Beaverly-Cowie, 26, Clyde Street, Edinburgh; Frank Evershed, care of Messrs. Clarke, Nicholls, and Coombs, Victoria Park, N.E.; and George Taylor, 6, Vicarage Park, Plumstead, S.E.

Certificates were read for the second time in favour of Messrs. Claude L. L. Claremont and Harold Douglas Elkington.

The following papers were read and discussed:—

"*Waldemar Fischer's Modification of Volhard's Method for the Volumetric Estimation of Manganese and its Comparison with other well-known Methods.*" By Edward Cahen, A.R.C.Sc., F.I.C., and Harry F. V. Little, A.R.C.Sc., B.Sc.

This modification of Volhard's method has been thoroughly examined, and its accuracy tested on samples of ferro-manganese, the manganese in which for comparison has been estimated by three other well-known methods, viz., the Bismuthate Process, the Basic Acetate Gravimetric Separation, and Pattinson's Standard Bichromate Method. Concordant results were obtained with all four methods.

"*Composition of British Wines.*" By Edward Russell and T. R. Hodgson.

The authors give analyses of a number of samples of British wine, the percentages of proof spirit in which vary from 19·5 to 25·6 per cent.

"*New Volumetric Process for the Estimation of Tungsten.*" By E. Knecht and E. Hibbert.

When tungstic acid is acted upon by zinc in strong hydrochloric acid solution it is reduced quantitatively to the condition of WCl_4. If a standard solution of iron alum be now added to the reduced solution, the colour of the latter passes from brown to blue and from blue to colourless. The disappearance of the blue marks the end-point, this being coincident with the oxidation of the WCl_4 to WO_3. Potassium sulphocyanide may also be used as indicator, the end-point being indicated by the appearance of the red colour. When the tungsten is present only in small amount, the sulphocyanide indicator is preferable.

The results obtained by the new process on pure tungstic acid and tungstate of soda show that it is expeditious and accurate. It is further shown that the reaction is not interfered with by the presence of iron. Details are given of the application of the process to the valuation of ferro-tungsten.

"*New Volumetric Process for the Estimation of Molybdenum.*" By E. Knecht and F. W. Atack.

Molybdic acid is reduced by zinc and strong hydrochloric acid to the condition of $MoCl_3$. The reduced solution thus obtained cannot be titrated with iron alum as in the preceding case, since sulphocyanide yields an intensely coloured compound with the reduced molybdenum solution, which obscures the end-point. By employing in place of iron alum a standard solution of methylene blue a definite end-point is obtained, the contents of the flask acquiring a blue colour coincident with the formation of $MoCl_5$. The method as tested on pure molybdic acid and on ammonium molybdate was found in all cases to give accurate results. The presence of iron does not interfere with the estimation of the molybdenum, so that the process can be employed for molybdenum steels and for ferromolybdenum. Further work is being done with a view to adapting the process to the estimation of phosphorus.

"*Degree of Accuracy with which Proteins can be Estimated in Milk by Aldehyde Titration.*" By H. Droop Richmond.

A series of careful comparisons showed that the aldehyde figure multiplied by 0·170 gave results agreeing with the proteins deduced by multiplying the total nitrogen by 6·38, within the limits +0·20 and − 0·13 per cent.

A very abnormal sample, however, containing a large proportion of albumin showed an error of 0·5 per cent.

"*Gorgonzola Cheese.*" By Edward Hinks.

In twenty samples of cheese there was present a mineral coating amounting, in addition to the natural rind, to from 16 to 27 per cent of the whole weight of the cheese. The mineral was natural barytes, and the composition of eight of these coats was (mean)—Barytes, 83·6 per cent; fat (tallow), 15·6 per cent; moisture, 0·8 per cent. The thickness of the coats was from $\frac{3}{16}$ ths to $\frac{4}{16}$ ths of an inch.

In early part of 1910 coated cheese amounted to about 50 per cent of whole imports. No difference exists in manufacture of cheeses, whether coated or not.

"*Tests for Cocaine and certain Cocaine Substitutes.*" By E. H. HANKIN.

The author has studied the permanganate test for cocaine. If carried out in the improved manner described in the paper it is one of great delicacy and constitutes a ready means of distinguishing between cocaine and certain cocaine substitutes, such as stovaine, alypin, tropacocaine, and scopolamine.

"*Analyses of Hevea Latex.*" (Abstract). By CLAYTON BEADLE and HENRY P. STEVENS.

The analysis of latex made by Faraday is erroneously quoted as that of Hevea latex—while it is probably Castilloa latex.

Analyses are given showing the specific gravity and composition of latex obtained from the bark of trees four years old, trees ten years old, and from the petioles of leaves. The latex analysed was free from added water, and was the average product from at least one hundred trees. Figures are also given illustrating the variation in percentage of total solids with the manner and frequency of tapping.

NOTICES OF BOOKS.

Analytical Chemistry. By F. P. TREADWELL, Ph.D. Authorised Translation by WILLIAM T. HALL, S.B. Vol. II. *Quantitative Analysis.* Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1910.

THE second English edition of Treadwell's "Analytical Chemistry" is based upon the fourth German edition, to the text of which some additions have been made by the translator to render the book more useful to English-speaking students. As a standard authority on quantitative analysis the second volume ranks with the most comprehensive in the English language. The new matter includes directions for the separation of calcium and magnesium, the determination of zinc and manganese as pyrophosphates, and methods involving the use of dimethylglyoxime for the estimation of cobalt. The section on volumetric work is, as in the earlier edition, particularly full and detailed; stress is laid upon the need for applying corrections for temperature in volumetric analysis, in which a high degree of accuracy is required, and the use of the true litre rather than Mohr's litre is advocated. The table of chemical factors has been re-calculated for the new edition from the values for the atomic weights given in the International Table for 1910.

Engineering Chemistry. By THOMAS B. STILLMAN, M.Sc., Ph.D. Fourth Edition. Easton, Pa.: Chemical Publishing Co. London: Williams and Norgate. 1910.

THE fourth edition of this text-book of quantitative analytical chemistry, which is intended chiefly for the use of engineering students and chemists, has been brought up to date in matters of detail, and a considerable amount of new material has been added. The technology of coal, for example, is treated much more fully than before, and the section on pyrometry, which is a subject in which progress has been very rapid recently, has been carefully revised. New methods of softening boiler water are described, and an important article on acetylene, written by R. E. Brückner, the chief engineer of the Commercial Acetylene Company of New York, has been added. The book contains copious references to standard works on the subjects of which it treats, and although possibly it aims at being too comprehensive it is a work which will be found of real assistance to the technical student.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cli., No. 11, October 31, 1910.

Preparation of Argon.—Georges Claude.—The 96 per cent oxygen obtained from liquid air contains normally 3 per cent of argon, which can be isolated by absorbing the oxygen by means of copper and the nitrogen by red-hot magnesium. With the author's apparatus 3 litres of oxygen can be treated per minute, and thus 4—6 litres of argon are obtained per hour for two hours, after which time the copper is used up.

Analysis of Fatty Substances by Separating Solid Fatty Acids from Liquid Acids.—M. David.—The ammoniacal salts of the solid fatty acids are quite insoluble at 13—14° in a large excess of liquid ammonia, while the ammoniacal salts of the liquid acids are completely soluble. Thus, if a mixture of acids is dissolved in alcohol, excess of ammonia is added, and the mixture is heated to 14—15°, the salts of stearic, palmitic, oxystearic, iso oleic, lauric, and arachic acids remain undissolved, and can be directly determined by treating the residue with warm hydrochloric acid.

Synthesis of Ketones of Tetrahydroaromatic Series.—G. Darzens and H. Rost.—Cyclohexane when treated with normal butyryl chloride in presence of aluminium chloride gives *n*-butyrylcyclohexane, and other ketones of the tetrahydroaromatic series can be obtained similarly; from the ketones the authors have prepared other hexahydroaromatic derivatives.

Verbascose, a New Sugar.—Em. Bourquelot and M. Bridel.—From the root of *Verbascum Thapsus*, L., the authors have isolated a new sugar to which they have given the name verbascose. When hydrolysed it gives lævulose, glucose, and galactose, and it is thus analogous to stachyose, of which it may be an isomer. It has a higher melting-point than stachyose (220° instead of 170°) and a greater rotatory power (+169·9° against +148·9°).

Sterilisation of Large Quantities of Water by Ultra-violet Light.—M. Urbain, Cl. Scal, and A. Feige.—Large quantities of water can readily be sterilised by ultra-violet light if each molecule of liquid is made to pass before the source of light in the same direction and at the same rate. This may be effected by making the water flow spirally through a cylindrical vessel, in the middle of which the source of light—an arc lamp—is placed.

MISCELLANEOUS.

Royal Institution.—On Thursday next, December 29, at 3 o'clock, Prof. Silvanus P. Thompson will commence the Christmas Course of six juvenile lectures at the Royal Institution on "Sound, Musical and Non-musical" (a Course of Experimental Acoustics).

Borough Polytechnic Institute.—The prospectus of the Borough Polytechnic Institute for the Session 1910—1911 gives full particulars of the work which is carried on in the Institute. Many new evening and other classes have been arranged, and some special courses of lectures on the Chemistry and Manufacture of Food Stuffs and on the Analysis of Laundry Trade Materials. The Institute is doing a valuable work in putting higher technical instruction within the reach of both men and women students, and the prospectus shows that it is rapidly extending its activity in all directions.

MEETINGS FOR THE WEEK.

THURSDAY, 29th. / SATURDAY, 31st. — Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Sound, Musical and Non-musical" (a Course of Experimental Acoustics), by Prof. Silvanus P. Thompson, F.R.S., &c.

THE CHEMICAL NEWS.

Vol. CII., No. 2666.

AN INVESTIGATION INTO THE CAUSES OF THE DIFFERENCES IN THE ACTION OF SODIUM AND POTASSIUM ON WATER.

By MANINDRANATH BANERJEE,
Professor of Chemistry, Bengal Technical Institute.

Experimental.

(a) *With Sodium.*

When a small piece is thrown on water it—

1. Floats and forms a round symmetrical white globule.

2. Makes a hissing sound.

3. Briskly swims to and fro.

4. Catches fire (emitting a bright *yellow* flame)—not ordinarily, but when kept steady by some way or other (as by means of a rod or being thrown upon thick starch solution.

5. Evolves hydrogen from all sides, which can be collected and tested.

6. Makes the water acted upon greasy or soapy to the touch and alkaline to test-paper.

7. Finally, disappears completely.

(b) *With Potassium.*

When a small piece is thrown on water it—

1. Floats, but does not form a round globule; or if it at all forms, it is hardly visible.

2. Makes a hissing sound. The action is more violent than that of sodium.

3. Does not swim briskly like sodium.

4. Catches fire at once (*i.e.*, just when it is thrown on water), emitting a *violet* flame.

5. Evolves hydrogen gas from all its sides, but this cannot be collected owing to its immediate explosion with air, due to the violent action of K on water.

6. Makes the water acted upon greasy or soapy to the touch and alkaline to test-paper.

7. Finally, disappears completely.

	Potassium.	Sodium.
1. Atomic weight	39	23
2. Specific gravity	0·855	0·972
3. Molecular volume	45·2	24
4. Vapour density	19·5	11·46
5. Heat of combination with oxygen	97,000 cals.	100,000 cals.
6. Product	K_2O	Na_2O
7. Specific gravity of product	2·8	2·3
8. Molecular volume of product.	35·5	22·1
9. Evolution of heat on dissolving	45 000 cals.	42,500 cals.
10. Product formed	KOH	NaOH
11. Specific gravity of product	2·19	2·13
12. Molecular volume of product	27	18·5
13. Degree of solubility of product..	Not very easily soluble.	Easily soluble.
14. Heat of solution at 18° C.	13,290 cals.	9940 cals.

Distinction between the Two Reactions.

The distinction between the two reactions is clear from the results tabulated above. *Potassium* acts more violently on water than *sodium*, showing that the former gives indications of more energy in combining with water than sodium. There is some clear difference between the reactions as evidenced from the following:—*Sodium*, when thrown upon water, forms a round symmetrical globule which can be distinctly seen, while with *potassium* no such thing is visible. *Sodium* moves briskly to and fro just on getting into water, while with *potassium* no such brisk movement is observed. With *sodium* no yellow flame is visible except when it is brought to a standstill, while in the case of *potassium* the hydrogen evolved ignites with a violet flame at once, *i.e.*, the moment after it is thrown upon water.

The action of potassium on water is called violent because of its bursting into flame immediately after it is thrown on water. The cause of such violence of action is sought for in the explanation that the affinity of potassium for water is greater than that of sodium, and this affinity is explained as being due to the *quantity of heat* developed in combination, as also to the *character of the products* formed. The decomposition of water by potassium and sodium in this case is said to be depending upon the energy of combination of potassium and sodium with oxygen forming K_2O and Na_2O, which is represented by the heat units developed during the reaction, viz., 97,000 and 100,000 calories respectively. K_2O and Na_2O dissolve in water with the evolution of 45,000 calories and 42,500 calories, forming KOH and NaCH, and the heat of solution exceeds in the case of potassium by 3350 calories, though the degree of solubility in case of the former is slightly less than that of the latter. The heat developed in the case of potassium is sufficient, as is often said, to inflame the hydrogen.

Argument.

The explanation hitherto set forth for the cause of these differences in the two reactions of sodium and potassium on water, viz., that these are dependent on the quantity of heat developed in combination as also upon the character, specially the degree of solubility of the product formed, seems to be quite incomprehensible in the face of all the experimental results we have obtained, inasmuch as the quantity of heat developed in case of sodium on water has been found to be 3000 calories greater than that of potassium, and K_2O is less soluble in water than Na_2O. Mendeleeff asserts "the energy of the action of K on water is explained by the fact that K_2O evolves more heat than Na_2O in combining with water." These are represented by 45,000 and 42,500 calories. While accepting that this evolution of a greater amount of heat by 2500 calories in case of potassium has something to do with the violence of action of potassium on water, it cannot definitely indicate the true cause of the difference in the two reactions, viz., of K and Na on water. For example, the heat developed, as results of observation show, in both the cases are quite sufficient to ignite the hydrogen evolved; but in case of potassium the heat developed ignites the hydrogen evolved, while in case of sodium it remains inoperative. The cause of this, as has hitherto been set forth, is that with sodium the heat dissipates owing to its brisk motion. This might be accepted as true, but this dissipation of heat is the effect of some other cause which has not been cleared up. It is put forward that the evolution of hydrogen from *sodium* from all its sides with uniform rapidity sets the metal in motion. While this can equally be said of *potassium*, the results of experiments prove that, in case of this metal, the hydrogen evolved fails to move it to and fro on water.

Conclusion.

From all our observations of nearly 200 experiments performed we have arrived at this conclusion, that the true cause of this brisk movement on water in case of *sodium* is its *low vapour density* (11·5), its *low molecular volume* (24),

as well as the *low density and molecular volume* of Na_2O (23 and 22·1), and of NaOH (2·13 and 18·5); these factors in case of *potassium* being 19·5, 45·2, 2·8, 35·5, 2·19, 27, respectively (*vide* Table above).

When potassium and sodium are thrown on water the hydrogen that is evolved from all sides is generally, as is indicated by the colour of the flame, charged with the vapours of the metals, and hence the densities of these vapours are responsible for their motion to and fro over the liquid. The metals themselves remain, owing to the great amount of *heat generated* in the reaction, in the *spheroidal state*, and hence easily capable of being set to motion by any other force. The density of *sodium vapour* is nearly half as low as that of *potassium* (Na = 11·5, K = 19·5), the density of K_2C has been found to be 2·8, while that of Na_2O 2·3; the molecular volume of K_2O is 35·5, while that of Na_2O 22·1; the density and molecular volume of KOH and NaOH are 2·19 and 2·13 respectively. The consideration of these facts plays, no doubt, the most important *rôle* in explaining the differences of the reactions of K and Na on water. In case of K the high density and a very larger molecular volume of its vapour counteract the motion of the H evolved from all sides, and hence its movement is considerably retarded. The great amount of heat which is liberated is thus prevented from being dissipated, and therefore it bursts into flame. In case of Na the density, &c., being very low the hydrogen evolved keeps it in a state of motion, the heat generated becomes thus dissipated, and hence the gas does not ignite.

Calcutta, November 27, 1910.

ANALYSIS OF CAPE GOOSEBERRY.

By W. KING.

THE Cape gooseberry is a sub-erect plant, native to South America. The fruit is enclosed in a large inflated calyx, and is about the size and shape of a cherry. When ripe it attains a greenish amber colour. It is largely used in South Africa for making jams and preserves. The following figures show that its chief value as a food lies in its content of sugar, which constitutes about 55 per cent of the total solids :—

Water	82·61
Sugars	9·59
Woody fibre	2·04
Protein	2·68
Acidity as citric acid	1·69
Oil..	1·23
Ash	0·82
	100 66

The sugars consisted of 6·46 per cent cane-sugar and 3·13 per cent fruit sugar. The acids were principally citric, but included tartaric and malic acids. The ash contained 54 per cent of potash.

Government Laboratory, Durban,
October 29, 1910.

Qualitative and Quantitative Determination of Arsenic Acid in presence of Arsenious Acid by means of Magnesium Mixture. J. C. Brünnich and F. Smith. —Arsenic acid can be determined in presence of arsenious acid by means of magnesium mixture if the solution does not contain much more than 0·5 per cent of As_2O_3. There must not be more alkali salt in the solution than the amount corresponding to about 1 per cent of NaOH. A very dilute ammoniacal magnesium mixture must be used containing 5·5 per cent $MgCl_2.6H_2O$, 10·5 per cent NH_4Cl, and 1·4 per cent NH_3. Ammonia must not be added.—*Zeit. Anorg. Chem.*, lxviii., No. 4.

THE DETERMINATION OF TOTAL SULPHUR IN ORGANIC MATTER.*

By HERMAN SCHREIBER.

Introduction.

A GREAT many methods have been proposed for the determination of total sulphur in organic matter, but probably only two of these are either easy to manipulate or accurate, namely the Barlow-Tollens, or absolute method (*Journ. Am. Chem. Soc.*, 1904, xxvi., 341), and the Osborne, or peroxide method (*Bull.* 107, Revised, p. 23, U.S. Dept. Agr., Bureau of Chemistry). When the latter is applied to solid material, however, it leaves much to be desired in the way of ease of manipulation and speed, and has absolutely no claim to exactness of detail. It is true that the water used for moistening the sample is measured, and the sodium carbonate is weighed, but the amount of sodium peroxide added varies with the material analysed, and with the rate at which the reagent is added. The amount of acid which must be added after fusion is also an unknown factor; it varies in each case, which necessitates making the solution alkaline again and then acid. These, however, are not all of the difficulties encountered. The fusions have a tendency to burn and blow out of the crucible, and this happens most frequently when the determinations must be rapidly made, for the peroxide method has a dignity all its own and will brook no haste or impatience. All of these objections were keenly realised when it became necessary to make about 100 sulphur determinations in a recent research.

An ideal method for this determination should embody several features. First, it must not call for excessive amounts of reagents, nor such as will interfere with the precipitation of the barium sulphate or contaminate the precipitate; second, the reagents employed must serve two purposes, *i.e.*, they must destroy all of the organic matter, and all of the sulphur must be fixed and oxidised to sulphate; third, the method must be fairly rapid and not require a large amount of practice, so that an analyst can make the determination from time to time without great delay and difficulty.

It is difficult to outline a method which will meet all of these conditions, but after making quite a number of experiments the following procedure was evolved, which seems to fulfil the requirements more nearly than the peroxide method.

The Proposed Method.

Weigh 1 grm. of material in a nickel crucible of 100 cc. capacity, add 10 cc. of a solution made by dissolving 100 grms. of sodium nitrate and 150 grms. of sodium hydrate in 500 cc. of water. Then add 5 grms. of crystallised magnesium nitrate, and stir with a platinum rod, making sure that the mass is thoroughly mixed, and that the sample is broken up as much as possible. Wash down the material adhering to the stirring-rod and sides of the crucible with the smallest possible amount of water. (This is essential since the addition of much water will prolong the subsequent heating unnecessarily). Heat for one hour on a hot plate covered with a thin sheet of asbestos paper, keeping the temperature at about 130° C. Then put the cover on the crucible, tilting it in such a fashion as to leave an opening for the steam to escape, and heat further for one hour at from 150° to 160° C., or until the material is entirely dry. If the fusions begin to bump, lower the heat so that the covers will not be jarred down tight on the crucibles, and the material lost by frothing. When the mass is entirely dry, put the covers on tight, and heat gradually until the temperature reaches 180° C., then heat for thirty-five minutes, maintaining the temperature at about 180° to 200° C. These temperatures were determined by laying the thermometer down on the hot plate.

* *Circular* No. 56, United States Department of Agriculture, Bureau of Chemistry.

TABLE I.—COMPARISON OF THE RESULTS BY THE PEROXIDE AND BY THE PROPOSED METHOD FOR THE DETERMINATION OF TOTAL SULPHUR.

No. of sample.	Description of sample.	Peroxide method (*a*). Amount of sample.	Peroxide method (*a*). First precipitation. Sulphur.		Peroxide method (*a*). Re-precipitation (*b*). Sulphur.		Proposed method (*a*). Amount of sample.	Proposed method (*a*). First precipitation. Sulphur.		Proposed method (*a*). Re-precipitation (*b*). Sulphur.		Peroxide method averages. A. Before fusion.	Peroxide method averages. B. After fusion.	Proposed method averages. C. Before fusion.	Proposed method averages. D. After fusion.	Difference between columns B and C (B − C).
		Grms.	Grm.	Per cent.	Grm.	Per cent.	Grms.	Grm.	Per cent.	Grm.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1.	White of egg..	1·0035	0·0162	1·61	—	—	1·0045	0·0151	1·50	—	—	1·64	—	1·54	—	—
		0·9955	0·0166	1·67	—	—	1·0025	0·0159	1·58	—	—					
2.	White of egg..	0·9978	0·0167	1·67	—	—	1·0015	0·0145	1·45	—	—	1·67	—	1·49	—	—
		1·0025	0·0167	1 67	—	—	0·9995	0·0153	1·53	—	—					
3.	White of egg..	1·0148	0·0163	1·61	—	—	1·0100	0·0160	1·58	—	—	1·64	—	1·58	—	—
		1·0330	0·0172	1·67	—	—	1·0075	0·0158	1·57	—	—					
51.	White of egg..	1·0110	0·0153	1·51	—	—	1·0055	0·0139	1·38	—	—	1·49	—	1·35	—	—
		1·0035	0·0146	1·46	—	—	1·0160	0·0133	1·31	—	—					
54.	White of egg..	1·0046	0·0131	1·30	—	—	1·0045	0·0133	1·32	—	—	1·35	—	1·29	—	—
		1·0000	0·0138	1·38	—	—	1·0023	0·0125	1·25	—	—					
	Blank	—	0·0017	—	—	—	—	0·0004	—	—	—	—	—	—	—	—
A.	Mustard (ground)	1·0015	0·0124	1·24	0·0122	1·22	1·0105	0·0120	1·19	0·0111	1·10	1·24	1·22	1·19	1·10	+0·03
		1·0030	0·0124	1·24	0·0122	1·22	1·0035	0·0119	1·19	0·0111	1·10					
B.	Mustard (ground)	1·0040	0·0130	1·30	0·0128	1·28	1·0050	0·0146	1·45	0·0124	1·23	1·28	1·28	1·32	1·22	−0·04
		1·0255	0·0128	1·25	0·0130	1·27	1·0050	0·0118	1·18	0·0121	1·20					
C.	Mustard (ground)	1·0025	0·0128	1·28	0·0120	1·20	1·0040	0·0120	1·20	0·0111	1·10	1·26	1·22	1·21	1·10	+0·01
		1·0075	0·0124	1·23	0·0124	1·23	1·0213	0·0125	1·22	Lost	—					
D.	Mustard (ground)	1·0135	0·0158	1·56	0·0157	1·55	1·0120	0·0133	1·32	0·0137	1·35	1·52	1·51	1·40	1·37	+0·11
		1·0000	0·0147	1·47	0·0146	1·46	1·0060	0·0148	1·47	0·0139	1·38					
E.	Mustard (ground)	1·0080	0·0142	1·41	0·0140	1·39	1·0017	0·0133	1·33	0·0124	1·24	1·35	2·34	1·32	1·17	+0·02
		1·0035	0·0129	1·29	0·0128	1·28	1·0000	0·0131	1·31	0·0109	1·09					
	Blank	—	0·0009	—	0·0011	—	—	0·0004	—	0·0007	—	—	—	—	—	—
7931.	Valve rubber..	1·0000	0·0435	4·35	0·0426	4·26	1·0135	0·0435	4·29	0·0417	4·12	4·35	4·27	4·27	4·10	0·00
		1·0155	0·0441	4·34	0·0432	4·27	0·9990	0·0425	4·25	0·0407	4·07					
7934.	Valve rubber..	1·0000	0·0438	4·38	0·0430	4·30	1·0075	0·0415	4·12	0·0397	3·94	4·35	4·26	4·21	3·95	+0·05
		1·0025	0·0432	4·31	0·0422	4·21	1·0055	0·0432	4·30	0·0397	3·95					
7935.	Valve rubber..	1·0045	0·0324	3·23	0·0305	3·04	1·0045	0·0286	2·85	0·0276	2·75	3·19	2·92	2·88	2·77	+0·04
		1·0040	0·0316	3·15	0·0281	2·80	1·0075	0·0292	2·90	0·0281	2·79					
7937.	Valve rubber..	0·9990	0·0435	4·35	0·0428	4·28	1·0055	0·0417	4·15	0·0401	3·99	4·30	4·21	4·14	3·99	+0·07
		1·0010	0·0425	4·25	0·0414	4·14	1·0035	0·0413	4·12	0·0400	3·99					
8136.	Tubing	1·0040	0·0846	8·43	—	—	1·0230	0·0805	7·87	0·0771	7·54	8·44	8·38	7·82	7·50	—
		1·0080	0·0852	8·45	—	—	1·0660	0·0827	7·76	0·0794	7·45					
		—	—	—	—	—	1·0035	0·0798	7·95	—	—	—	—	8·02	—	—
		—	—	—	—	—	1·0135	0·0820	8·09	—	—					
	Tubing (*c*) ..	—	—	8·12	—	—	—	—	—	—	—	8·06	—	—	—	—
		—	—	8·00	—	—	—	—	—	—	—					
	Blank	—	0·0022	—	0·0028	—	—	0·0002	—	0·0000	—	—	—	—	—	—

(*a*) Results given have been corrected for blank.
(*b*) After fusing barium sulphate with sodium carbonate.
(*c*) Determination by E. W. Boughton, Contracts Laboratory.

Now set the crucible (with the cover on tight) into a round hole in a piece of asbestos board, so that about 1·5 inches of the lower part of the crucible shall project below the asbestos board as Lunge has directed, the asbestos board to be laid flat ("Chemisch-Technische Untersuchunge Methoden," 1904, i., 428). Heat with the Bunsen burner for half-an-hour, allowing the flame to just touch the bottom of the crucible during the first fifteen minutes, and then with the full heat during the last fifteen minutes. (Never let the inner cone of the Bunsen burner strike the crucible). During the first five minutes of heating with the full flame keep the crucible in an upright position, then remove the cover, and tilt the crucible so as to fuse any material which may have crept up the sides. Then return the crucible to the upright position, replace the cover, and heat for five minutes more. When the fusion has solidified, and before it has entirely cooled, place the crucible in a 600 cc. beaker with 150 cc. of distilled water, and cover with a watch-glass. Put the crucible cover in the beaker, beside the crucible, and slightly rotate and tilt the beaker so that all parts of the crucible shall be touched by the water. Run in 13 cc. of hydrochloric acid (specific gravity 1·19) from a burette, and again rotate the beaker slightly. Tip the crucible so that the other side comes in contact with the acid liquor, allow it to stand a few minutes, and remove the crucible and cover, washing the liquid adhering to them back into the beaker by means of distilled water. Any fused material adhering to the sides of the crucible can easily be removed with a stirring-rod. Place the beaker on the steam-bath, and heat for about half-an-hour, and then let it stand in the cold over-night. Filter and wash the insoluble residue. Heat the filtrate on the steam-bath or otherwise, and precipitate with a 10 per cent barium chloride solution.

In all of the determinations here reported the solutions were precipitated by heating on the steam-bath, adding 10 cc. of barium chloride to the solution quickly, and stirring as soon as the precipitate began to form. After adding the barium chloride the solutions were allowed to remain on the steam-bath about one hour, and were then removed to the table, and stood in the cold over-night, after replacing any water lost by evaporation. All filtrations, except the solution of the fusions of the barium sulphate with sodium carbonate, were filtered through S. and S. blue ribbon filter-paper. The fusions of the barium sulphate were filtered through white ribbon filter-paper, and all precipitates were washed with cold water.

In this method a crucible loses from 0·3 to 1·3 grms. of its weight in each determination, an average of 0·9 grm. as calculated from 20 determinations. By the peroxide method the crucible loses from 1·2 to 2 grms. of its weight in a fusion, an average of 1·4 grms. based on 13 determinations. Using a griddle hot-plate, 14 by 18 inches, 18 fusions can easily be made in a day. The only way in which a determination can be lost is by heating too rapidly on the hot-plate, thus causing it to boil over or splatter.

Description of Samples and Analytical Results.

Total sulphur was determined by both the peroxide method and the proposed method on five samples of dried white of eggs, three of which were made from the same lot of eggs by boiling with various amounts of copper sulphate, washing free of copper, and drying and grinding; one was a sample of commercial dried albumin, and one was the white of eggs boiled in the shell, dried, and ground. Sulphur was also determined on four samples of mustard seed and one sample of ground mustard. A is pure white mustard, B is black mustard containing 64 per cent of charlock, C is commercial ground mustard, D is pure brown mustard, and E is commercial ground seed. These samples were furnished by the Microchemical Laboratory. Sulphur was also determined on five samples of vulcanised rubber furnished by the Contracts Laboratory.

The 60 determinations were made without repeating any, except No. 8136, unless a loss occurred by the leaking of the crucible. This happened in three instances only, so that the work represents fairly well the results which the two methods will give under the same conditions without repetition and selection of results. Twelve determinations were made at a time with each kind of material, two determinations on each sample, and two blanks. The results obtained are given in Table I. The peroxide fusions were not hurried, but were allowed to fuse for three or four hours. No. 8136 is a sample of rubber-tubing which was not ground very finely, and which had been found to contain about 50 per cent of free sulphur. These facts probably account for the discrepancies in the determination.

Discussion of Results.

Skinner (*Bull.* 116, p. 92, U.S. Dept. Agr., Bureau of Chemistry), comparing the Barlow-Tollens and peroxide methods, found that the latter gave slightly higher results in five out of seven cases, the difference averaging about +0·11 per cent of SO_4 or +0·036 per cent of sulphur. The proposed method gives sulphur results about 0·1 per cent lower than the peroxide method; the average of the 12 values which were lower by the proposed method would thus be about 0·064 per cent less than by the absolute method. Both of these discrepancies are well within the experimental error. Also it should be noted that the difference between the figures obtained by fusing the barium sulphate in the peroxide method and re-precipitating, and those resulting from the first precipitation by the proposed method (as given in Columns B and C, Table I.) varies from −0·04 to +0·11 per cent. In six out of twelve cases the figures obtained by the first precipitation in the proposed method are nearer the values obtained by fusing and re-precipitating the barium sulphate in the peroxide method than they are to the results of the first precipitation in the peroxide method. The peroxide method gives a very high blank as compared to the proposed method; with the former this blank amounted to from 0·009 to 0·0028 per cent of sulphur, and in the latter it amounts to from 0 to 0·0007 per cent. As the blanks by the peroxide method are very high an error would be introduced if they were not run in each set. This is very clearly demonstrated in the determinations of sulphur in sulphuric acid solutions as given in Table II.

Sulphuric Acid Solutions.

To determine the effect of the salts in solution on the precipitation of sulphuric acid, fusions were made by the peroxide method, and by the proposed method, definite volumes of dilute sulphuric acid being added to the solutions and blanks run at the same time. The fusions were made exactly as in the case of the total sulphur determinations given in Table I. Then they were dissolved, an excess of 2 cc. of hydrochloric acid was added, the solution was filtered, and the measured amount of dilute sulphuric acid added. The sulphuric acid was precipitated with barium chloride solution in the same manner as in the other determinations. The results are given in Table II.

TABLE II.—*Determination of Sulphur in Dilute Sulphuric Acid Solutions by four different Methods.*

Quantity of solution used.	By precipitating from distilled water after adding 2 cc. excess of concentrated hydrochloric acid.	By weighing as ammonium sulphate by Lunge's method.	By precipitating from a solution containing a fusion—	
			By the proposed method.	By the peroxide method.
	Grm.	Grm.	Grm.	Grm.
10 cc. of Sol. A	0·0140	0·0142	0·0141	0·0127
	0·0141	0·0142	0·0141	0·0147
25 cc. of Sol. A	0·0352	0·0350	0·0362	0·0340
	0·0351	0·0349	0·0361	0·0355
10 cc. of Sol. B	0·0799	0·0795	0·0832	0·0811
	0·0800	0·0796	0·0832	0·0805
Blanks (*a*) ..	—	—	0·0001	0·0024

(*a*) Corrected for in values given.

The proposed method gives results 0·1 per cent too high when 3·5 per cent of sulphur is in solution, and 0·3 per cent too high when 8 per cent of sulphur is present. This occlusion of salts evidently compensates for an error which would cause the result to be low, as can be seen from Table I. and the experimental data.

Lunge and Stierling found similar conditions in the precipitations of sulphuric acid in aqueous solution and in the presence of salts. The quick addition of the barium chloride solution gave erroneous data in aqueous solution, and correct results in the presence of salts, while the slow addition of the precipitant gave just the opposite.

The proposed method employs about 7·6 grms. of salt (calculated as chlorides), and the peroxide method 15 grms. or more.

Preliminary Experiments.

The preliminary experimental work leading up to this method consisted in testing the various reagents which have been proposed in methods for the determination of sulphur, varying the temperature, reagents, and time and manner of treatment. The 22 experiments made involved 160 single determinations, exclusive of those that were lost on account of faulty manipulation or seemed valueless from the nature of the reaction.

Determinations were made by using mixtures of reagents composed of from 1·25 to 3 grms. of sodium hydroxide, 5 to 15 cc. of water, 0·5 to 1 grm. of sodium carbonate, 1 to 2 grms. of sodium nitrate, 1 to 3 grms. of magnesium oxide, and from 3 to 10 grms. of crystallised magnesium nitrite.

The treatment of the material with the reagents varied from drying on the steam-bath and burning, to heating at from 80° to 230° C. for from one a-half to five hours before burning. By these means values were obtained which ranged, for instance, from 1·13 to 1·45 per cent of sulphur on a sample which contained 1·56 per cent by the peroxide method, and from 3·91 to 4·50 per cent on a rubber containing 4·17 per cent by the peroxide method. Of 75 determinations, each the average of two duplicates, the peroxide value was the highest except in three instances. When the preliminary heating was continued for from two and a-half to five hours, rising above 175° C. for at least thirty minutes of that time, it was noticed that the values usually approached the peroxide value by 0·1 per cent.

These preliminary determinations all indicate that adding reagents in solution, drying, and then ashing causes a loss of sulphur, and that the substance must receive a definite preliminary heating before the sulphur can be absorbed by the alkaline reagent. This was noted after repeated experiments had been made with modifications of Eschka's method, and it seemed probable that when the alkaline reagent was added in solution, the mixture dried down, and a coating consisting of an alkaline oxidising medium was formed, all of the sulphur would be absorbed. This idea was substantiated by subsequent experiments.

Potassium salts were not tried in any of the experiments, as Lunge and Stierling have found that potassium chloride dissolves twice as much barium sulphate as sodium chloride does (see "The Determination of Sulphuric Acid by means of Barium Chloride in the presence of Interfering Substances," Sixth International Congress of Applied Chemistry, *Report*, 1906, p. 347). The use of sodium carbonate was discontinued after the twelfth experiment, as Barlow has shown that, as far as the absorption of sulphur is concerned, soda can be omitted when magnesia is present (see "Losses of Sulphur on Charring," *Journ. Am. Chem. Soc.*, 1904, xxvi., 354).

The values obtained by these different methods rarely approached those by the peroxide method nearer than 0·1 per cent, which suggests that the latter may be too high. It was therefore decided to examine a new lot of samples by the peroxide method, fuse the barium sulphate obtained with soda, re-precipitate, and determine the sulphur by the proposed method. The results obtained are given in Table I.

It appears that the first precipitation of the sulphuric acid by this method gives values very nearly approaching those obtained by fusing the barium sulphate obtained by the peroxide method and re-precipitating. The differences between the two sets of results thus obtained range from −0·04 to +0·11 per cent (an average of 0·04 per cent) as given in the last column of Table I.; these differences are within the experimental error.

REPORT ON GASEOUS COMBUSTION.*

By WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S.

(Concluded from p. 311).

Section VI.—*The Influence of Hot Surfaces upon Combustion.*

It is to the genius of Sir Humphry Davy that we owe the discovery of surface combustion. In his experiments on the ignition-points of various gases he had found, what is now a matter of common knowledge, that the constituents of a combustible mixture will combine with fair velocity at temperatures below the ignition-point. This led him to ask the question whether, seeing that the temperatures of flames far exceed those at which solids become incandescent, a metallic wire can be maintained at incandescence by the slow combination of two gases without actual flame. He therefore tried the effect of introducing a warm platinum wire into a jar containing a mixture of coal-gas and air rendered non-explosive by an excess of the combustible constituents. The wire immediately became red-hot, and remained so until nearly the whole of the oxygen had disappeared. In subsequent experiments, Davy proved that hydrogen is far more susceptible to surface combustion than either ethylene or carbon monoxide; also, that the power of inducing surface combustion is by no means confined to the metals of the platinum group, which, however, exhibit it in an eminent degree.

In 1823 the subject was systematically investigated by Dulong and Thénard, and independently also by Döbereiner, who showed that all solids possess the power of accelerating combustion in varying degrees according to their specific characters and fineness of division. Two years later William Henry observed that when a platinum ball is immersed in a mixture of equal volumes of ethylene and electrolytic gas the hydrogen and oxygen alone combine, no combustion of the hydrocarbon occurring unless the original mixture contains a much larger proportion of oxygen. This important result was confirmed by Thomas Graham in 1829.

Several explanations of surface combustion were put forward by these early investigators. Davy himself suggested an electrochemical one. "Supposing," he wrote, "oxygen and hydrogen to be in the relation of negative and positive, it is necessary to effect their combination that their electricities should be brought into equilibrium or discharged. This is done by the electrical spark or flame, which offers a conducting medium for this purpose, or by raising them to a temperature in which they become themselves conductors. Now platinum, palladium, and iridium are bodies very slightly positive with respect to oxygen. . . . They offer to the gases the conducting medium necessary for carrying off and bringing into equilibrium their electricities without any intervening energy, and accumulate the heat produced by this equilibrium." Döbereiner, who discovered that freshly prepared platinum black absorbs oxygen from the air, and that in this "oxygenated" condition it will cause steam to be formed on being plunged into a jar of hydrogen, contended that the metal merely acts as a carrier of oxygen. On the other hand, Fusinieri (1825) maintained that it is the combustible gas (hydrogen) only which is affected by the

* Read before the British Association (Section B), Sheffield Meeting, 1910.

surface, being condensed and rendered extraordinarily active by association with the surface.

The matter formed the subject of a celebrated controversy between Faraday and De la Rive in 1834-35. De la Rive strongly upheld the view that surface combustion essentially consists of a series of rapidly alternating oxidations and reductions of the catalysing material. Faraday, whilst not denying that finely divided platinum absorbs oxygen, argued with great force that true surface combustion involves an action quite distinct from that of an oxidised wire or foil upon upon a combustible gas. The function of the solid is, he contended, to condense both the oxygen and the combustible gas at the surface, thus producing a condition in the surface layer comparable to that of high pressure. After the year 1836, however, interest in the subject waned, and was not revived until quite recently.

It may here be remarked that heated surfaces have undoubtedly a marked influence in accelerating not only combustion but all chemical interchanges in gaseous systems. It is usually considered that the action of the surfaces is merely an accelerating and not a directive one at any particular temperature, and although this may be generally true it is not necessarily or universally so. But in regard to combustion it may be assumed that, in general, the introduction of a hot surface will merely accelerate the process.

In the generation and applications of gaseous fuels the technologist has to deal not only with combustion, and the interaction of the products of incomplete combustion, but also with decomposition and dissociation phenomena, and contact with hot surfaces accelerates all alike. Thus the influence of hot solids—in the shape of furnace walls and the like—assumes an importance which can hardly be over-estimated.

It will be generally agreed that the best means of elucidating the factors operative in surface combustion lies in determining the rates of combination of different gases with oxygen when the reacting mixtures are brought into contact with various solid surfaces at selected constant temperatures. This has been the line of attack usually adopted in recent investigations. But the method is only capable of yielding results of any value when the temperature selected is low enough to prevent the masking of the effects of surface combustion proper by changes in the main body of the gas, which is not in contact with the surface at any given instant.

In interpreting the results of such velocity measurements the following possible factors must be considered—namely, (1) the actual rate of combination at the surface, (2) the rates at which the reacting gases respectively diffuse inwards from the outside mixture on to the surface, (3) the rate at which the reaction product is removed from the surface, (4) the rates at which the reacting gases (or either of them) are rendered "active" by the surface, supposing that the surface may act in some such manner, and (5) changes (if any) in the physical texture of the surface itself.

It is obvious that, since any system in which a gaseous mixture is combining exclusively at the surface of a heated solid must be regarded as heterogeneous, the velocity of reaction will not be governed by its "order," as would probably be the case with a homogeneous system. Nevertheless several recent investigators, notably Bodenstein in his earlier experiments upon the non-explosive combination of electrolytic gas in contact with the walls of a glazed porcelain vessel (*Zeit. Phys. Chem.*, 1899, xxix., 665), by overlooking this obvious consideration have largely invalidated their conclusions.

Of the factors above enumerated it is now generally agreed among competent observers that the actual rate of combination at the surface far exceeds either the rates of diffusion of the reacting gases on to the surface or the rates at which they are rendered "active" by the surface. This being so, it follows that the amount of change observed in the system in unit time will not be governed by the actual rate of combination at the surface, but by one or other of the remaining factors, whichever happens to be the slowest in its operation.

Nernst, who has recently advanced a general theory of reactions in hetereogeneous systems, based on measurements of the rates of solution of salts in water, or of such substances as magnesia in acids, ignores (in the case of surface combustion) the possible "activation" of the gases by the surface, and contends that the velocity of surface combustion is governed by diffusion factors only. Thus he has written :—

"Da diese Reaktionen wohl ausschliesslich an der Grenzfläche des Katalysaten abspielen, so wird die Geschwindigkeit keineswegs durch den Mechanismus der betreffenden Reaktion, sondern wenn, was allerdings von vornherein nicht sicher ist, der Katalysaten während des Reaktionsverlaufes konstante Beschaffenheit behält und zugleich mit praktisch unendlicher Geschwindigkeit die betreffenden Substanzen an der Grenzfläche zur Reaktion bringt, auch hier lediglich durch die Diffusion der reagierenden Stoffe zum Katalysaten bendingt werden" (*Zeit. Phys. Chem.*, 1904, xlvii., 55).

Bodenstein (*Zeit. Phys. Chem.*, 1903, xlvi., 725), in an entirely inconclusive series of experiments on the combination of hydrogen and oxygen in contact with platinum at the ordinary temperature, attempted to provide an experimental basis for the above theory, but it has been recently completely disproved by the researches of the writer and his pupils (R. V. Wheeler, G. W. Andrew, A. Forshaw, and H. Hartley), a first instalment only of which has so far been published (Bone and Wheeler, "The Combination of Hydrogen and Oxygen in Contact with Hot Surfaces," *Phil. Trans.*, 1906, A. 206, i.). The following is a brief *résumé* of the principal results of these researches :—

At an early stage of the research it became manifest that, in order to avoid errors inherent in a too restricted view of the phenomena, the action of a considerable variety of surfaces must be studied, including (1) such ordinarily non-oxidisable metals as gold, silver, and platinum, (2) oxidisable metals, such as copper and nickel, (3) easily reducible oxides, as well as (4) non-reducible oxides of both basic and acidic character. Although the investigation has revealed certain minor differences between the action of the various surfaces, the results as a whole leave no room for doubt but that the catalytic combustion depends primarily upon the condensation or absorption of one or other (and possibly both) of the reacting gases by the surface, whereby they are rendered "active." Any chemical explanation—such, for instance, as the supposition of a rapidly alternating series of oxidations and reductions of the catalysing surface—is inconsistent with the numerous velocity measurements made during the research. Equally certain is it that the rate of combustion is governed, not by diffusion factors, as Nernst has supposed, but by the rate of "activation" of one of the reacting gases (and usually of the combustible gas) by the surface.

The catalysing power of a new surface at a given temperature usually increases up to a steady maximum when successive charges of the reacting gases, mixed in their combining ratios, are circulated over it ; after the attainment of this steady condition, the rate of combination is always directly proportional to the pressure, provided that the gases are present in their combining ratios and the product of combustion is rapidly removed from the sphere of action. Where, however, one or other of the reacting gases is present in excess, the rate of combustion is in nearly all cases proportional to the partial presence of the combustible gas (*e.g.*, hydrogen or carbonic oxide), which thus becomes the ruling factor. The behaviour of copper oxide towards mixtures of hydrogen with excess of oxygen, and of nickel oxide towards mixtures of carbon monoxide with excess of oxygen, have so far proved exceptional in this respect, the observed rates in both cases being more nearly proportional to the partial pressure of the oxygen than to that of the combustible gas. In the case of copper

oxide there is definite proof of the formation of a condensed film of "active" oxygen at the surface, which actually burns up the hydrogen before it can reach the still more active oxygen chemically combined with the copper.

The catalysing powers of all the metallic and non-reducible oxide surfaces examined are highly stimulated by previous exposure to the combustible gas, which is undoubtedly rendered "active" by association with the surface. This stimulus is usually very durable, but in most cases it is at once destroyed by a short exposure to oxygen. Although as a general rule oxygen has *per se* no stimulating effect on a catalysing surface, cases to the contrary have been encountered; but even in these exceptional instances the effect is neither so marked nor so durable as the corresponding effects always observed in respect of the combustible gas.

One notable feature with regard to the catalytic combustion of carbon monoxide over a fireclay surface is the fact that the rate of combustion of a mixture $2CO + O_2$ at 500° is about doubled by a thorough drying of the gases, the "reaction constant" increasing from about 0·09 to about 0·20. This remarkable result can hardly be explained on the supposition that, in the case of the undried mixture (saturated at 18°), steam acts merely as a diluent: it apparently exercises a specific retarding influence out of all proportion to its relative mass.

Of scarcely less interest are some recent results bearing upon the effects of a hot fireclay surface (at 500°) upon the relative rates of combustion of methane, hydrogen, and carbon monoxide. In the previous section attention was directed to the fact that in ordinary explosive combustion the affinities of methane and other hydrocarbons far exceed those either of hydrogen or of carbon monoxide for oxygen. In contact with a hot surface, however, the order is completely reversed, owing to an apparently selective action of the surface in rendering the combustible gases active. This circumstance is sufficient to invalidate the conclusions of certain earlier investigators, notably those of Landolt ("Uber die chemischen Vorgänge in der Flamme des Leuchtgas," Habilitationsschrift, Breslau, 1856), concerning the relative combustibilities of various gases, owing to their having sucked off the products of partial combustion from the inner regions of coal-gas flames through platinum tubes and the like. It may be taken for granted that the introduction of a hot solid into a mixture of burning gases is in itself sufficient to upset the regular conditions of explosive combustion.

The conclusions drawn by Bone and Wheeler (*loc. cit.*) as to the catalytic combustion of hydrogen derive collateral support from the recent researches of Sabatier and Senderens on the remarkable powers of many metallic surfaces (and especially nickel) of rendering this gas "active" at comparatively low temperatures. In illustration of their results may be quoted the following remarkable instances of direct "hydrogenations" effected by merely passing a mixture of the substance in question with hydrogen over finely divided and freshly reduced nickel. In this way olefinic hydrocarbons are convertible into the corresponding paraffins at 160°; benzene yields cyclohexane; nitro-benzene may be reduced to aniline; whilst nitro-methane is convertible into methylamine at 150° to 180°, and into methane and ammonia at 350°. Finally, a mixture of carbon monoxide (1 vol.) and hydrogen (3 vols.) may be completely transformed into methane and steam at 250°.

In the present imperfect state of our knowledge any suggestion which may be put forward as to the action of hot surfaces in rendering such gases as hydrogen or carbon monoxide "active" must be considered as quite tentative. Several facts, however, point to a possible connection between surface combustion and the emission of charged particles by hot solids. In 1903 H. A. Wilson (*Phil. Trans.*, A, ccii., 243) discovered that hydrogen has an enormous influence upon the negative leakage from a clean platinum wire at high temperatures; thus at 135°, for a given potential difference, the leakage in hydrogen at 0·014 mm. pressure was found to be no less than 25,000 times greater than in air; it was also proportional to the pressure and depended upon the hydrogen actually occluded by the metal. These observations have since been confirmed by O. W. Richardson (*Phil. Trans.*, 1908, A, ccvii., 1)—who, however, finds that the leakage consists of two parts, one proportional to the pressure (due to ionisation by collisions) and the other independent of it; he takes the view that hydrogen does not act *per se*, but only indirectly by producing some change in the surface of the metal.

Sir J. J. Thomson has found that the rate of emission of negative corpuscles by alkali metals at ordinary temperatures is greatly increased whilst they are absorbing hydrogen (*Phil. Mag.*, 1905. 6th series, x., 584), and F. Horton has proved that the negative leakage from hot lime is much greater in hydrogen than in air (*Phil. Trans.*, 1908, A, ccvii., 149).

With regard to the catalytic combustion of hydrogen in contact with metallic surfaces P. J. Kirkby, in experimenting upon the effects of electrically heating a platinum wire to *circa* 275° in electrolytic gas at pressures under 40 mm., concluded that it is "probably connected with the corpuscular discharge which is known to be emitted by platinum" (*Phil. Mag.*, 1905, 6th series, x., 467). Finally, it has recently been proved in the writer's laboratory that gold gauze immediately acquires a negative charge on its inducing the surface combustion of either hydrogen or of carbon monoxide. All these facts point to the necessity of a systematic investigation of the electrical condition of heated surfaces during catalytic combustion as a preliminary to a better understanding of the phenomenon.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 1st, 1910.

Prof. Harold B. Dixon, M.A., Ph.D., F.R.S., President, in the Chair.

Messrs. F. S. Long and Horace Finnemore were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Albert Ashe, Laurie Square, Romford; Morris Cutner, B.Sc., 21, Bairstow Street, Preston; James Edward A. Devlin, Marist Brothers College, Uitenhage, Cape Colony; William Temple Gardner, Bruern, Alexandra Road, Upper Parkstone; Harold James Page, Avondale, Meteor Road, Westcliff-on-Sea; Robert Viner Stanford, M.Sc., Ph.D., Cardiff City Mental Hospital, Whitchurch, Glam.

A ballot for the election of Fellows was held, and the following were declared duly elected:—Malcolm Percival Applebey; Manindranath Banerjee; Fred Wilkinson Barwick; Sarat Chandra Bhattacharya, M.A.; Stewart McGregor Bosworth, B.Sc.; André Bracher; Frederick Hugh Rochfort Brady; John C. Briggs; Henry Vincent Aird Briscoe, B.Sc.; John Brown, B.Sc.; Bertram Hayward Buttle; Frank Anthony Camp; Frederick Challenger, B.Sc., Reginald Thomas Colgate; Thomas Watts Coslett; Marshall Perley Cram, A.M., Ph.D.; David Chalmers Crawford, M.A., B.Sc.; Charles Crichton; John Hughes Davies, B.Sc., Ph.D.; Arthur Dodd; James Hugh Duncan; William Gidley Emmett, B.A.; Ainslie Jackson Ensor, B.Sc.; John George Finlayson, B.A.; George Alexander Goddon; Count Arnaud de Gramont; Fred. Holt, B.Sc.; Prince Mahmood Ali Khan, B.A.; Edmund Knecht, M.Sc., Ph.D.; William Arthur Knight, M.A.; Bertram Lambert, M.A.; Alleyne Leechman; Kenneth Stewart Low; Clement Ward Lowe; David Jackson

MacGeorge; Malcolm McNish; Rikō Majima; James Irvine Orme Masson, M.Sc.; Thomas R. Merton, B.Sc.; Alec Duncan Mitchell, B.Sc.; Dhirendranath Mitra, B.A.; Harold Moore, B.Sc.; James Eckersley Myers, B.Sc.; Valliyll Govindan Nair, B.A., B.Sc.; Sidney Herbert Newman, B.Sc.; John Hamilton Paterson, M.Sc.; Alfred John Pennington; Benjamin Ashwell Posford; Hari Prasad, B.A.; Frederick Valentine Ramsden; Alfred Oswald Ransome; Thomas John Rees, B.A., B.Sc.; Gangaram Rajendrarao Rele; Joseph Ridgway, B.A.; James Beglar Robinson; Rajendra Nath Sen, M.A., M.Sc.; Frederick Herbert Sharpe; Percy Lancelot James Smith, M.A.; William James Pittock Smith; Jwala Prasad Srivastava, B.Sc.; Claude Vareille Temperley, B.Sc.; Augustus George Terrey; Leo Tschugaeff; Richard Babington Turbutt, B.A.; Joseph Turner; John Fleming Culun Brown Vance; Robert Lauder Mackenzie Wallis, B.A.; Arthur Bernard Williams; Herbert Goulding Williams, B.Sc.; William Norman Stewart Wright; Syed Muhammad Yusuf, B.Sc.

Of the following papers, those marked * were read:—

*321. "*The Triazo-group.* Part XV. *Triazoethylene (Vinylazoimide) and the Triazoethyl Halides.*" By Martin Onslow Forster and Sidney Herbert Newman.

Triazoethylene (vinylazoimide), $CH_2{:}CHN_3$, prepared by the action of hot alcoholic potassium hydroxide on triazoethyl bromide or iodide, is a pale yellow liquid, boiling at 26°/760 mm. The dibromide is rapidly decomposed by cold water, yielding bromo-acetaldehyde with hydrazoic and hydrobromic acids.

β - Chloro - α - triazoethane (triazoethyl chloride), $N_3{\cdot}CH_2{\cdot}CH_2Cl$, obtained from triazoethyl iodide by heating it with mercuric chloride, boils at 45°/25 mm., and has D_{24} 1·2885. *β-Bromo-α-triazoethane (triazoethyl bromide)*, $N_3{\cdot}CH_2{\cdot}CH_2Br$, arising from triazoethyl alcohol and phosphorus tribromide, boils at 49°/20 mm., and has D_{19} 1·6675. *β-Iodo-α-triazoethane (triazoethyl iodide)*, $N_3{\cdot}CH_2{\cdot}CH_2I$, produced when a solution of sodium iodide in dry acetone acts on the foregoing substance, boils at 68°/20 mm., and has D_{25} 1·9154.

β-Triazoethyl ether, $N_3{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$, is the result of heating triazoethyl alcohol with ethyl iodide and dry silver oxide; it boils at 49°/25 mm., and has D_{24} 0·9744.

Discussion.

The President asked Dr. Forster whether he had attempted to heat the vapour of triazoethylene, and, if so, whether it had exploded.

Dr. T. Callan inquired whether the authors had tried the action of silver azide on triazoethyl iodide with a view to obtaining, by simple replacement of the iodine by the triazo-group, a compound with two triazo-groups in the molecule.

Dr. Forster stated that the vapour of triazoethylene had not been heated; nor had any attempt been made to effect interaction between triazoethyl iodide and silver azide, because the symmetrical bistriazoethane which should arise could be prepared by a more simple process and had already been examined.

*322. "*The Dinitro-derivatives of Dimethyl-p-toluidine.*" By Gilbert T. Morgan and Arthur Clayton.

Although dimethyl-*p*-toluidine, when nitrated in concentrated sulphuric acid solution, yields only 2-nitrodimethyl-*p*-toluidine, yet when the nitration mixture is poured into water so that the temperature rises to 40°, the reaction proceeds a stage further, and 2 : 5-dinitrodimethyl-*p*-toluidine (m. p. 103—104°) is produced. The position assumed by the second nitro-group in this compound was ascertained in the following manner.

2-Nitrodimethyl-*p*-toluidine, when reduced and acetylated, yielded 2-acetyl-4 : 4-dimethyl-2 : 4-diaminotoluene, which, on nitration, gave *5-nitro-2-acetylaminodimethyl-p-toluidine*. On reduction, this nitro-compound furnished *2-acetyl-2 : 5-diaminodimethyl-p-toluidine*, which, by the agency of the Sandmeyer reaction, gave rise to 5-bromo-2-acetylaminodimethyl-*p*-toluidine, the constitution of which has already been determined.

The foregoing 2-acetyl-2 : 5-diaminodimethyl-*p*-toluidine was converted into 2 : 5-diacetyldiaminodimethyl-*p*-toluidine, which can also be prepared by reducing 2 : 5-dinitrodimethyl-*p*-toluidine and acetylating the resulting 2 : 5-diaminodimethyl-*p*-toluidine, thus demonstrating the position of the second nitro-group in 2 : 5-dinitrodimethyl-*p*-toluidine. *2 : 6-Dinitrodimethyl-p-toluidine* (m. p. 192°), was prepared by the action of methyl sulphate on 2 : 6-dinitro-*p*-toluidine.

Discussion.

Dr. Flürscheim mentioned that Crum Brown and Gibson's rule, which did not profess to explain the directing influences in the benzene nucleus, had also ceased to correspond with facts (compare *Journ. Prakt. Chem.*, 1902, [2], lxvi., 322). He had also proved that the alternate hypothesis advocated by Dr. Morgan - the prevention of ortho-para-substitution by the negativity of a substituent—also did not agree with facts (compare *Journ. Prakt. Chem.*, 1902, [2], lxvi., 329; 1905, [2], lxxi., 500).

On the other hand, he had himself suggested a solution based on the varying strength of "single" bonds (compare *loc. cit.*, and *Journ. Prakt. Chem.*, 1907, [2], lxxvi., 197, for directing influence of methyl; also *Ber.*, 1906, xxxix., 2015), and this had been borne out by every observed fact. The sole exception had hitherto been Dr. Morgan's suggestion (*Proc.*, 1910, xxv., 82) that, in dilute acid, a second nitro-group entered 2-nitrodimethyl-*p*-toluidine and possibly in the 6-position. The experimental decision had been left to him and Mr. Clayton, and their results had vindicated his (the speaker's) theory.

Dr. Morgan, in reply, said that they regarded the nitration phenomenon from a mechanical standpoint, based on the Pope and Barlow theory of the configuration of benzene, whereas Dr. Flürscheim, in looking at the matter rather from the point of view of Kekulé's benzene formula, laid too much stress on the connection between unsaturation of the substituent radicle and its power of inducing ortho-para-substitution. But although the unsaturated groups, NH_2, OH, &c., induced substitution in the ortho-para-positions, yet the methyl radicle did the same, and the latter group could not fairly be assumed to possess much residual affinity.

On the other hand, he regarded the groups, $-NH_3{\cdot}HSO_4$, $-NH_2R{\cdot}HSO_4$, and $-NHR_2{\cdot}HSO_4$, present when aromatic amines were nitrated in concentrated sulphuric acid, as being distinctly unsaturated complexes owing to the presence of double linkings in the sulphate group—

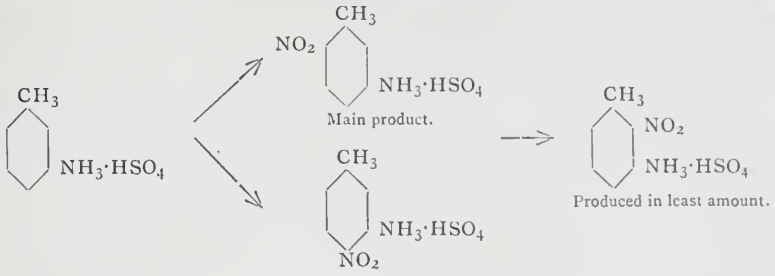
$$C_6H_5{\cdot}NH_3{\cdot}O{>}S{\overset{=}{=}}O \quad HO{>}S{\overset{=}{=}}O.$$

Nevertheless, these complexes did not usually induce substitution in ortho-para-positions, but in meta-positions. Where the latter positions were not assumed, as in the case of *m*-toluidine, the exceptional orientation could be traced to the influence of other substituents (Noelting and Stoecklin, *Ber.*, 1891, xxiv., 564). (See next page).

In this nitration, the nitro-groups took up the positions they would assume even in the absence of the $NH_3{\cdot}HSO_4$ radicle, this result indicating that the directive (attractive) influence of the saturated methyl group prevailed over the influence of the sulphate complex, the repulsive effect of which was observed only in the fact that 6-nitro-*m*-toluidine was the chief product.

*323. "*Experiments on the Walden Inversion.* Part VI. *Conversion of the Optically Active α-Hydroxy-α-phenylpropionic Acids into α-Chloro-α-phenylpropionic Acids.*" By Alex. McKenzie and George William Clough.

The authors find that thionyl chloride and phosphorus pentachloride behave differently towards *l*-α-hydroxy-α-phenylpropionic acid, inasmuch as the former gives *l*-α-chloro-α-phenylpropionic acid, whereas the latter gives *d*-α-chloro-α-phenylpropionic acid. The action of thionyl



chloride and of phosphorus pentachloride on optically active ethyl α-hydroxy-α-phenylpropionate has also been examined.

324. "*The Auto-reduction of Hydrazines.*" By Frederick Daniel Chattaway and Montague Aldridge.

Aromatic hydrazines, when heated, undergo simultaneous oxidation and reduction, whereby an amine, ammonia, nitrogen, and a hydrocarbon are produced, according to the equation: $2R{\cdot}NH{\cdot}NH_2 = RNH_2 + NH_3 + N_2 + RH$.

The reaction is a general one, and, in the case of unsubstituted primary hydrazines, such as phenylhydrazine, the tolylhydrazines, and the naphthylhydrazines, takes place quantitatively. It proceeds slowly even at the boiling temperature, the rate increasing rapidly as the boiling-point of the hydrazine is approached. It is thus impossible to obtain any hydrazine in a state of purity by distillation.

The slow decomposition which hydrazines undergo on keeping, even when air is excluded, is due to this auto-reduction.

In the case of hydrazines containing a substituted aromatic residue, although this primary decomposition takes place to a considerable extent, other reactions may also occur on heating, especially at a high temperature, due to the presence of the substituting atoms or groups.

325. "*The Activity of Acids as Catalysts in Relation to the Nature of the Solvent Medium.*" By Harry Medforth Dawson.

The influence of the nature of the solvent on the rate of the tautomeric change of acetone, in presence of sulphuric acid as a catalyst, has been investigated in alcohol-water mixtures ranging from pure water to anhydrous alcohol. It is found that the velocity of the tautomeric change is nearly independent of the composition of the solvent if this contains less than about seventy volumes per cent of ethyl alcohol. As the proportion of alcohol is increased, the reaction velocity increases, slowly at first, but afterwards more and more rapidly, until in anhydrous alcohol the speed is more than one hundred times as great as it is in aqueous solution. The large changes in velocity are probably due to changes in the catalytic activity of the acid in the different solvents. Although the velocities in alcohol and in water differ to such a very large extent, the concentrations of the positive acid ions in equimolar acid solutions appear to be very nearly equal, and it is supposed that the actual catalyst is represented by free hydrogen ions, which, however, in consequence of their relatively small concentration, play only a subsidiary part in connection with the electrical conductivity of the solutions.

326. "*The Volume of a Solute in Solution.*" By Dan Tyrer.

The volume changes which occur on the dissolution of a solute have been measured, and the specific solution volume of the solute has been calculated by means of the equation—

$$v = \frac{(100+A)S_1 - 100S_0}{A},$$

where v is the specific solution volume, or the change in volume caused by the dissolution of 1 grm. of the solute, A the percentage concentration of the solution, S_1 the specific volume of the solution, and S_0 that of the pure solvent. The values of S_1 and the values of v, calculated according to the above equation, have been determined for a large number of solutions of various solutes and solvents by means of the dilatometer and pyknometer.

Normal organic solutes and solvents have been used to avoid complications through molecular association or dissociation. It has been found that (1) the specific solution volume is, in most cases, constant and quite independent of the concentration, (2) the specific solution volume of the solute varies but slightly from solvent to solvent.

The cause of the variations with change of solvent was discussed, and the hypothesis was put forward that through an increase or decrease in the molecular attraction between the molecules of solvent and solute, a contraction or expansion of the solvent occurs, causing a variation in the calculated specific volume of the solute in solution.

327. "*The Absorption Spectra of some Derivatives and Isomerides of* 1 : 2-*Diketo*-Δ^3-cyclo*pentene.*" By John Edward Purvis.

The results of this investigation show that (1) the colour is determined primarily by the monoketonic and diketonic structures; (2) the absorption in the more refrangible regions of the monoketonic compounds is determined by the type of ring in which the ketonic structure occurs; (3) in the diketonic compounds the colour is modified in the direction of the more refrangible regions by the introduction of an oximino- or :N·NHPh group, a result analogous to that previously observed in diketopyrrolines; (4) in the diketonic compounds the absorption of the phenylhydrazone or of the *iso*phenazine derivative is wholly different from that of the corresponding substances derived from the diketopyrrolines; (5) the difference in the *iso*phenazine compound and in a bluish coloured sodium derivative of 1 : 2-diketo-Δ^5-*cyclo*pentene is explained as the result of changes in the positional valencies of the ring.

328. "*4-β-Aminoethylglyoxaline (β-Iminazolylethylamine) and the other Active Principles of Ergot.*" By George Barger and Henry Hallet Dale.

The identification of an ergot base having a very powerful action on the isolated uterus as 4-β-aminoethylglyoxaline (β-iminazolylethylamine) (*Proc. Chem. Soc.*, xxvi., 128) has been completed by analysis of the dipicrate, and by a comparison of physiological properties. The method of isolation was described in detail.

329. "*Synthesis of Camphoric Acid.*" By Gustav Komppa.

Although Thorpe (*Proc.*, 1909, xxv., 94) was able to obtain only a 10 per cent yield of methyl diketo*apo*camphorate, three of the author's assistants have obtained yields varying from 45 to 70·5 per cent.

From the methylated ester, which Blanc and Thorpe (*Trans.*, 1910, xcvii., 836) state to be the O-methyl ether, the author has now prepared, for the fifth time, *r*-dehydrocamphoric acid, and from this has obtained *r*-camphoric acid.

The author maintains the constitution previously assigned by him to methyl diketocamphorate, and shows that the methyl group in question must be attached to carbon and not to oxygen, as boiling hydriodic acid (Zeisel) fails to remove it.

330. "*Viscosity and Association.* Part I. *Association of the Phenols.*" By FERDINAND BERNARD THOLE.

The viscosities of a number of phenols and their derivatives have been measured both in the pure state and in solution. From the results, the following conclusions have been drawn:—

1. The results obtained by the viscometric method agree very closely with those derived from other physical constants, such as vapour pressure, dielectric constant, molecular surface energy, molecular refractivity, and molecular weight determined cryoscopically.

2. The viscosity determinations, using $\frac{\eta}{\text{mol. vol.}} \times 10^6$ as a criterion of association, show that phenols are associated, the ortho-compounds to the least, and the para-compounds to the greatest, extent. The ethers are not associated, but the acetates show slight association.

3. The carbethoxyl, aldehyde, nitro-, and halogen groups exert a marked inhibitive influence on association. Alkyl groups exert only a slight influence. Since the degree of inhibition of association appears to be intimately connected with the degree of unsaturation of the substituent, it is suggested that the depression of association is partly due to an attraction between the latent valency of the hydroxylic oxygen and the unsaturated substituent, the consequence being a diminution of the tendency to form complexes through the latent valency of the hydroxyl group. The same hypothesis explains the gradual disappearance of the characteristic reactivity of the carbonyl group in the series acetone-ethyl acetate-acetic acid.

4. Solution in even a comparatively non-dissociating solvent, such as amyl acetate, produces considerable disruption of the molecular aggregates. In a dissociating solvent, such as ethyl alcohol, the dissociation is practically complete.

331. "*Compounds produced by the Simultaneous Action of Nitrites and Hyposulphites on Nickel Salts. A Method for the Detection of Nickel in presence of much Cobalt.*" (Preliminary Note). By WALTER CRAVEN BALL.

When solutions of sodium or potassium nitrite and nickel nitrate are mixed, and sodium hyposulphite is gradually added, the liquid assumes the colour of a permanganate solution, and needle-shaped, dark purple crystals separate. This substance, of which the formula is possibly $Na_3NiNS_2O_8,4H_2O$, seems to be the sodium salt of a complex acid containing nickel. The potassium salt, similar in colour, but more soluble, may be obtained by a slight modification of the method. Both salts yield purple precipitates with barium and strontium solutions. Similar complex cyanides, of an intense reddish purple colour, may be obtained by treatment of the above substances with potassium cyanide, and also by the oxidation of ammoniacal solutions of hydroxylamine, containing a nickel salt and a cyanide. They are soluble in alcohol and other organic solvents, and afford a ready means of detecting nickel in presence of much cobalt.

The compounds are all very unstable, and from their method of preparation would appear to be derived from some compound intermediate between nitrous acid and hydroxylamine, possibly from dihydroxylamine.

Preparation of Metallic Radium.—E. Ebler.—Metallic radium can be prepared by slowly decomposing radium azide, $Ra(N_3)_2$, by heating. The author first proved that barium azide is not affected by radium rays. He then recrystallised barium radium azide, and gently heated; when the greater part of the radium mixed with the barium went over into the metallic state, still preserving its radioactive properties.—*Berichte*, xliii., No. 14.

NOTICES OF BOOKS.

Introduction to the Analysis of Drugs and Medicines. By BURT E. NELSON. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1910.

THE analyst who has not made a special study of drugs and medicines will find this book very useful, if he happens to be called upon to determine the ingredients of a medicinal mixture or the nature of a drug. The book is intended for the use of chemists and students who have had no experience in dealing with drugs, but possibly the author has erred in introducing rather an unnecessary amount of elementary matter. Thus, in the descriptions of general apparatus and the usual operations the illustrations of a microscope and a furnace might very well have been omitted. The usual methods of ultimate analysis, both inorganic and organic, are well described, and a good outline is given of the principles of drug analysis. The author has worked out a system which is a modification of Dragendorff's method, and which seems to be workable and practical. The drugs are divided by means of suitable reagents into six groups, and then the members of each group are separated by distinctive tests. Both Dragendorff's and Parsons's schemes are given in outline for reference. Microscopical analysis is treated shortly, and this section is illustrated by drawings which should materially assist the beginner in identifying a specimen. A very brief outline of pharmacological work is given, which is so sketchy as possibly to be hardly worth insertion. Among the tables at the end of the book is one very useful one in which all common organic substances used medicinally are tabulated in order of the amount of carbon in them, the full elementary analysis of each being given.

The British Journal Photographic Almanac, 1911. (Jubilee Issue). Edited by GEORGE E. BROWN, F.I.C. 1346 pages. Crown octavo, 7×5 inches. London: Henry Greenwood and Co.

THE "B. J. Almanac," as this annual publication is known among photographers of every English-speaking country, this year celebrates its Jubilee, and the publishers may reasonably point to its appearance as a record in technical journalism. The "Almanac," which in its current issue is a bulky volume weighing 2¾ lbs., had its beginning as a wall or sheet calendar, which was presented as a supplement to the *British Journal of Photography* in the year 1860. The five succeeding issues took the form of waistcoat-pocket volumes, containing such hints and brief information as sufficed for photographers in those days. The issue was enlarged to crown octavo size in the year 1866, since which date the "Almanac" has shown a steady increase in its number of pages, corresponding with the modern development of photography. For many years past it has supplied photographers with complete working instructions in the modern branches of the art, and has recorded in orderly fashion the technical progress made in each year. In the present volume a review of its past history is given, together with a number of portraits of editors and publishers, past and present.

Photographers "from China to Peru" look to the "Almanac" for practical information and for particulars of new apparatus and materials, and certainly the text and advertisement pages, which in the present fiftieth issue reach a total of 1346, leave no room for doubt that the amateur or professional worker finds the volume a veritable "Enquire Within upon Everything." The advertisement pages compete with those of the text in interest, as they contain the latest announcements of practically every photographic firm and the full price lists of a great many. Ready reference is provided to this great mass of information by the separate indexes, which are placed together at the end of the volume, and supply a key both to every item in the text and to every article advertised.

The London University Guide, 1911. London : University Correspondence College.

This guide contains the regulations for the degrees of London University, with many valuable hints upon text-books and the choice of subjects. In addition it contains an article on the constitution of the University, and a complete almanac showing the dates of all examinations, and of the issue of the class lists for the years 1910 and 1911. The guide is an invaluable possession for intending candidates for the examinations of the University, and gives full information as to the University Tutorial College, with tables of fees, names of tutors, and details of the various courses arranged for the benefit of its students.

Metropolitan Borough of Poplar. Annual Report for the Year 1909. By Fredk. Wm. Alexander.

The manufacture of electrolytic disinfecting fluid for use in the Poplar Baths has been a highly successful undertaking, and fuller details of its efficacy form an interesting part of this report. The fluid, which consists practically of a dilute solution of magnesium hypochlorite, is made very economically, and large quantities of it are given to the managers of sick asylums, boards of guardians, &c.; observation has shown that the water in the public baths is kept much cleaner and fresher by its use than is possible by other means.

Glass-blowing Applied to Laboratory Work. By Bernard D. Bolas. London : George Routledge and Sons, Ltd.; Dawbarn and Ward, Ltd.

This pamphlet gives a description of the tools which the glass blower and worker usually employs, and explains the methods of using them. Full accounts are also given of some of the simpler operations in glass working, and the directions are explicit enough to enable the student who follows them to acquire considerable dexterity in the manipulation of glass the inlaboratory.

South-Western Polytechnic Institute. Session 1910-1911. *Calendar and Prospectus of the Day and Evening College for Men and Women.*

The syllabus of the day and evening classes held at the South-Western Polytechnic indicates that the Institute is taking a prominent part in the furthering of higher scientific education in London, and the prospectus will repay the careful consideration of students who wish to complete for the science degrees of the University of London, or who want training in practically any branch of pure or applied science or domestic economy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xliii., No. 13, September 24, 1910.

Synthesis of Arsenic Hydride from its Elements.—A. C. Vournasos.—When a mixture of three parts of arsenic powder and 8 parts of dry sodium formate is heated to 400° a mixture of hydrogen and arsenic hydride is evolved. The equation is $6CH_2O_2Na + 2As = 3Na_2C_2O_4 + 2AsH_3$. Arsenic hydride can conveniently be prepared from sodium orthoarsenate and sodium formate :— $Na_3AsO_3 + 3CHO_2Na = 3Na_2CO_3 + AsH_3$. If the temperature is raised above 400° some carbon monoxide is evolved.

Direct Synthesis of Volatile Hydrogen Compounds.—A. C. Vournasos.—When heated with sodium formate the phosphides, sulphides, arsenic, and antimony derivatives of metals, also many chlorine, bromine, iodine, and fluorine derivatives, yield the corresponding halogen hydride. The same reaction occurs with selenides and tellurides. When amorphous silicon and anhydrous sodium formate are heated to 1300° hydrogen silicide is generated.

New Method of Preparing Nitriles of Fatty Series.—A. E. Arbusow.—The catalytic decomposition of aldehyde hydrazones in presence of copper chloride, platinum chloride, zinc chloride, and other salts gives varying yields of the nitriles of the fatty acids. Hydrazones with the smallest fatty radicles give very little nitrile, while those with larger radicles give good yields. Thus the phenyl hydrazone of isovaleraldehyde splits up in presence of copper chloride according to the equation $C_5H_{10}:N.NH.C_6H_5 = C_6H_5.NH_2 + C_5H_9N$.

Composition of Lead Ferricyanide.—Erich Müller and Otto Diefenthäler.—Two lead ferricyanide compounds have been described, $Pb_3[Fe(CN)_6]_2 + 16H_2O$ and $K_2Pb_2[Fe(CN)_6]_2 + 3H_2O$. When the former is precipitated from lead nitrate with potassium ferricyanide the proportion of lead to hydrogen ferricyanide is found to be Pb : $Fe(CN)_6$ = 2 : 1, and further investigation shows that its composition is probably $Pb_2[Fe(CN)_6]NO_3 + 5H_2O$.

Crystallisation of Fused Lead Silicates.—Siegfried Hilpert and Richard Nacken.—From previous investigations of the crystallisation of fused lead silicates solidified melts have been described as eutectic mixtures when they are really compounds characterised by very small maxima. Other similar compounds are calcium-*m*-ferrite and calcium aluminate, $5CaO.3Al_2O_3$. With the lead silicates the temperatures for eutectic crystallisation differ only very little from one another, and with the calcium silicates eutectic horizontals run at almost the same height throughout the whole diagram, but if it is assumed that silicic acid behaves towards chalk in the same way as towards lead oxide, the system $CaO.SiO_2$ is evidently thoroughly understood.

No. 14.

Preparation of Metallic Vanadium. — Wilhelm Prandtl and Benno Bleyer.—When a mixture of 100 parts of fused powdered V_2O_5, 49·5 parts of aluminium powder, and 20 parts of calcium fluoride is heated in a magnesia crucible, or better still, if the two first constituents are heated in a hollowed out mass of calcium fluoride, a vanadium regulus is obtained, the weight of which amounts to 70 to 80 per cent of the calculated weight. In spite of every precaution the vanadium metal thus prepared never contains more than about 95 per cent of vanadium, the residue consisting of oxygen.

Zirconium Earth and Erbium Earth from Titanate Mineral.—K. A. Hofmann.—The purest pieces of a euxenite examined by the author differed from a typical euxenite in containing a very large amount of titanium ; in composition they approximated to a titanate, $3TiO_2.2RO$, and they contained zirconium earth which gave unknown lines in the arc spectrum, and the equivalent weight of which was higher than that of the zirconium earth from zirconium silicate. The atomic weight of the neo-erbium from the erbium earth of the same mineral could be raised only from 167·43 to 167·68 by crystallisation of the acetylacetonate and the ammonium double oxalate as well as by the partial decomposition of the sulphate.

Adsorption of Acetylene by Palladium.—C. Paal and Christian Hohenegger.—Colloidal palladium has a greater power of adsorption for acetylene than for hydrogen, and when the ratio of the volume of acetylene adsorbed to one volume of palladium was determined it was found that it varied between wide limits, and evidently the phenomenon is one of adsorption only, no chemical compound being formed. Finely divided palladium also adsorbs acetylene.

Zeitschrift für Anorganische Chemie.
Vol. lxviii., No. 4, 1910.

Behaviour of Borax towards Zinc Salts in Aqueous Solution.—Friedrich Borchers.—When cold saturated borax solutions are precipitated with zinc salts (sulphate or chloride) the amount of boric acid entering into the precipitate increases with the concentration of the substances. The best yields of zinc borate are obtained if the solution of zinc salt is poured into the borax solution, and the borax is present in slight excess. Zinc sulphate or chloride must be used in as concentrated a form as possible, or in the solid state. From cold saturated solutions of borax the highest percentage of borax precipitated as zinc borate was 38·6 per cent. With supersaturated borax solution or with solid borax, zinc borate precipitates containing up to 83 per cent of the boric acid in the solution can be obtained. For pure borax solutions an excess of the precipitating reagent causes a diminished yield of zinc borate. Thus zinc borate is soluble in zinc sulphate, complex salts being formed. Other salts also act as solvents; *e.g.*, sodium chloride and magnesium chloride. Manganese chloride and sulphate also precipitate boric acid. By the addition of caustic soda OH-ions were introduced; these lowered the H-ion concentration of the zinc sulphate, and thus raised the borate concentration, but at the most only 70 per cent of the borax in the solution could be precipitated. If the zinc borate is removed by filtration and the filtrate is neutralised with caustic soda, and again precipitated with zinc salt solution, by repeating the process several times 94 per cent of the borax can be separated from the solution. Only very little borate is formed when free carbon dioxide is present in the cold saturated borax solution; if sodium carbonate is present the amount of precipitate is increased, but does not reach that obtained with an equivalent quantity of caustic soda. If caustic soda is added to solutions containing soda the solvent action of the zinc carbonate is diminished, and the formation of borate is increased. In borax solutions containing other salts, *e.g.*, NaCl and Na_2SO_4, besides Na_2CO_3, an excess of zinc salt is necessary in order to precipitate the greatest possible amount of borate.

Silver-sodium Alloys.—E. Quercigh.—From the study of the solidification curves of silver sodium alloys it is found that the two metals are miscible in all proportions in the liquid state. No compound is formed. There is a eutectic situated quite close to the sodium axis. The shape of the curve of the primary crystallisation shows that there is a tendency to form a compound, but when formed it must dissociate in the melt. Silver can dissolve up to 13 atoms per cent of sodium in the solid state.

Phosphorus Oxychloride as a Cryoscopic Solvent.—P. Walden.—Determinations of the freezing-point of pure phosphorus oxychloride show that this constant is incorrectly stated even in the standard text-books; it is neither −1·782° nor −1·5°, but lies above 0°. By fractional distillation and crystallisation a melting-point of +1·25° can easily be reached. Its cryoscopic constant is K = 76·8 (as compared with 69 given by Oddo). Using these new constants the molecular weights of iodine chloride, iodine cyanide, nitric acid anhydride, perchloric acid anhydride, and perosmic acid anhydride (osmium tetroxide) were determined, and it was found that phosphorus oxychloride is a dissociating medium, in which all these substances are contained in monomolecular solution; *i.e.*, as ClI, CNI, N_2O_5, Cl_2O_7, and O_8O_4.

Rôle of Water in Tremolite and some other Minerals.—E. T. Allen and J. K. Clement.—The investigation of different specimens of natural tremolite showed that they all contained from 1·7 to 2·5 per cent of water. This water is gradually given up as the temperature is raised without any loss of homogeneity and with only a very slight change in the optical properties. Thus the water is not chemically bound, although the powdered mineral is not completely dehydrated at 900°. It must be regarded as dissolved water and tremolite as a solid solution. A diopside from altered limestone contained 1 per cent of water, and behaved in practically the same way. Kupferrite and a specimen of beryl contained 3·8 and 2·5 per cent of water, which they gave up only very slowly at a comparatively high temperature (400—800°) without losing their homogeneity. It was not found possible to remove the water altogether. All these minerals show important resemblances to zeoliths, but differ from them in one way, viz., they do not give true equilibrium with water vapour at a low temperature. Fresh analyses show that all amphiboles contain water and also hornblendes, though in smaller quantity. Probably the amphiboles contain dissolved water as a characteristic constituent, and are solid solutions.

Quartz as a Geological Thermometer.—Fred Eugene Wright and Esper S. Larsen.—Quartz is capable of giving at least one, and possibly two, points for the geological thermometer scale, for when heated to 575° it undergoes an enantiotropic transformation into a second phase—Mugge's β quartz—while at 800° it is no longer stable at the ordinary pressure, but passes over into cristoballite. The transition-point of α and β quartz is determined by observing the sudden change of double refraction, circular polarisation, and coefficient of expansion at this temperature. The most accurate optical determinations fix the transition temperature at 575° ± 2. Crystallographic experiments enable a quartz which has been heated above 575° to be distinguished from one which has never reached this temperature.

Binary System of Alumina with Silicic Acid, Lime, and Magnesia.—E. S. Shepherd and G. A. Rankin.—Thermic experiments show that there is only one compound of aluminium and silicic acid (Al_2SiO_5) which is stable in contact with the melt; this is the mineral sillimanite. Andalusite and cyanite both go slowly over into sillimanite at 1300°. Four different compounds of aluminium and lime exist, viz.:—$3CaO.Al_2O_3$, $5CaO.3Al_2O_3$ of melting-point 1383°, $CaO.Al_2O_3$ of melting-point 1592°, and $3CaO.5Al_2O_3$. The first and last of these have no true melting-point, but the former is completely fused at 1555° and the latter at about 1730°. Two of these compounds, $5CaO.3Al_2O_3$ and $3CaO.5Al_2O_3$, have each an unstable form, while $3CaO.Al_2O_3$, and probably $3CaO.5Al_2O_3$, are unstable at the melting-point. It is probable that only $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ are present in Portland cement. Only one compound of alumina and magnesia exists, viz., $MgO.Al_2O_3$. Probably in the system MgO—CaO no compounds are present.

Equilibria in Lead Hydroxide Precipitations.—W. Herz.—The author tabulates the values of the constant of the law of mass action for the equation $PbCl_2 + 2KOH \rightleftharpoons Pb(OH)_2 + 2KCl$, and also the constants when ammonia and methylamine are used as the precipitating bases.

MEETINGS FOR THE WEEK.

Monday, Jan. 2nd. Society of Chemical Industry, 8. "Determination of Sucrose (Cane-sugar) in Sugar Factory Products by Clerget's Process using Invertase as Hydrolyst," by J. P. Ogilvie. "Testing of Incandescent Mantles," by J. H. Coste and W. E. F. Powney. "Radiation Errors in Flow Calorimeters," by J. H. Coste and B. R. James.

Tuesday, Jan. 3rd.
Thursday, „ 5th.
Saturday, „ 7th.
Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "Sound, Musical and Non-musical" (a Course of Experimental Acoustics), by Prof. Silvanus P. Thompson, F.R.S., &c.

Wednesday, 4th.—Royal Society of Arts, 5. (Juvenile Lectures). "A Study of Splashes, conducted by the Aid of Instantaneous Photography," by Prof. A. M. Worthington, C.B., F.R.S.

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